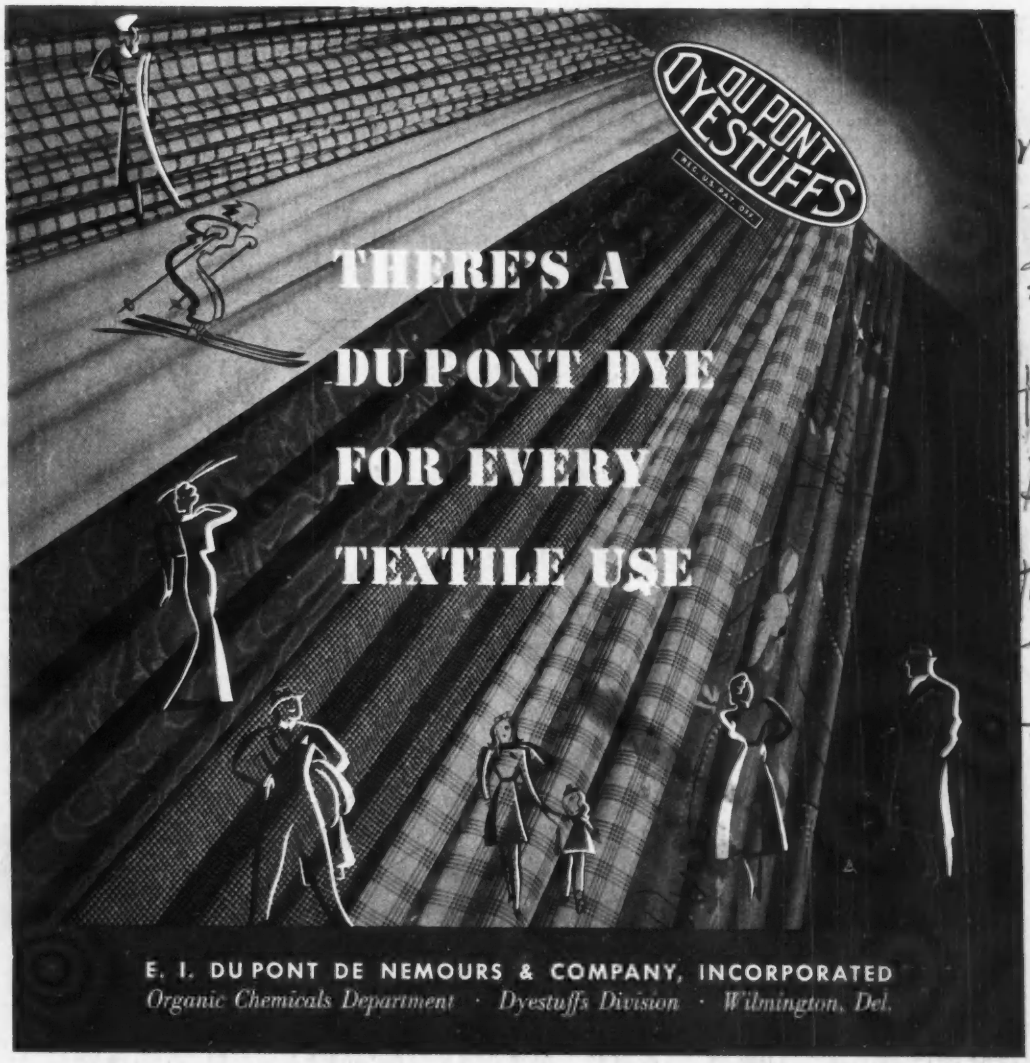
Quarterly Research Number

306.8
Am3

ARY
RECEIVED
APR 8 - 1938
U. S. Department of Agriculture

AMERICAN DYESTUFF REPORTER

VOLUME 27 APRIL 4, 1938 NUMBER 7


DU PONT DYESTUFFS
THERE'S A
DU PONT DYE
FOR EVERY
TEXTILE USE
E. I. DU PONT DE NEMOURS & COMPANY, INCORPORATED
Organic Chemicals Department · Dyestuffs Division · Wilmington, Del.

OFFICIAL PUBLICATION OF THE AMERICAN ASSOCIATION OF TEXTILE CHEMISTS AND COLORISTS

Nacconol

New Rapid Neutral Reliable

WOOL PROCESSING ASSISTANT

THE "ALL PURPOSE" SURFACE ACTIVE AGENT

Nacconol NR *An original, unique, super-safe, soap-free, organic detergent,* with the power and effectiveness in hard or soft water that gives you the strong, non-felting, scouring action so necessary for your work. Its efficient leveling and penetrating quality in the presence of acids, alkalis, or metallic salts will be a revelation.

Nacconol NR Try it for correcting dyeings on woolen piece goods when unevenness is encountered.

Nacconol NR You cannot afford to overlook this "all purpose" Surface Active Agent.

LET US SHOW YOU WHY!

NATIONAL ANILINE & CHEMICAL CO., Inc.

40 RECTOR STREET **NEW YORK, N. Y.**

BOSTON	150 Causeway St.	CHARLOTTE	201-203 W. First St.
PROVIDENCE	15 Westminster St.	GREENSBORO	Jefferson Standard Bldg.
CHICAGO	357 W. Erie St.	ATLANTA	140 Peachtree St.
PHILADELPHIA	200-204 S. Front St.	CHATTANOOGA	James Bldg.
SAN FRANCISCO	517 Howard St.	PORTLAND, ORE.	646 N. Thompson St.
TORONTO	137-145 Wellington St., West		

Branches and Distributors Throughout the World

PROCEEDINGS OF THE

American Association of Textile Chemists and Colorists

APRIL 4, 1938

Officers of the Association

ALBAN EAVENSON, *President*
Eavenson & Levering Co., Camden, N. J.

DUNCAN FERGUSON—ARTHUR R. THOMPSON, JR., *Vice-Presidents*

WILLIAM R. MOORHOUSE, *Treasurer*
National Aniline & Chemical Co., Boston, Mass.

HAROLD C. CHAPIN, *Secretary*
Lowell Textile Institute, Lowell, Mass.

LOUIS A. OLNEY
President Emeritus and Chairman of the Research Committee
Lowell Textile Institute, Lowell, Mass.

Councilors-at-Large

BERKELEY L. HATHORNE
G. R. KREMERS
WALTER M. SCOTT
HAROLD M. CHASE
ARTHUR E. HIRST
HAROLD DE WITT SMITH

Councilors Representing Sections

BEN VERITY (Rhode Island)
HANS MEYER (New York)
ROLAND E. DERBY (N. New England)
C. A. JONES (South Eastern)
R. M. RITTER (Philadelphia)
B. C. BLOWNEY, (Midwest)
HOMER WHELCHEL (South Central)
THOMAS R. SMITH (Piedmont)

Local Sections and Their Officers

Northern New England Section
Carl Z Draves, Chairman, Ludlow Mfg. & Sales Co., Ludlow, Mass.
Jonn N. Dalton, Secretary, Pacific Mills, Worsted Division, Lawrence. Mass

Rhode Island Section
Richard Haworth, Chairman, 25 Fountain St., Providence, R. I.
Raymond A. Pingree, Secretary, U. S. Finishing Co., Norwich, Conn.

New York Section
George L. Baxter, Chairman, Bradford Dyeing Association, 40 Worth St., New York, N. Y.
P. J. Kennedy, Secretary, E. I. duPont de Nemours & Co., Inc. 61 Thomas St., New York, N Y

Philadelphia Section
Herbert S. Travis, Chairman, Rohm & Haas Co., Inc., 222 West Washington Square, Philadelphia, Pa.
Paul L. Speakman, 1506 Delaware Ave., Wilmington, Del.

Piedmont Section
Raphael E. Rupp, Chairman, Pacific Mills, Lyman, S. C.
J. W. Ivey, Secretary, Mathieson Aikali Works, Inc., Charlotte, N. C.

South Central Section
Nestor Grotelueschen, Chairman, Magnet Mills, Clinton, Tenn.
W. S. McNab, Secretary, Quaker City Chemical Co., Knoxville, Tenn.

Midwest Section
Edward J. Siegrist, Chairman, Holeproof Hosiery Co., Milwaukee, Wis.
Herbert W. Tetzlaff, Secretary, Geigy Co., Inc., Milwaukee, Wis.

South-Eastern Section
Robert W. Philip, Chairman, Editor, "Cotton," Atlanta, Ga.
Alfred R. Macormac, Secretary, Alabama Polytechnic Institute, Auburn, Ala.

Lowell Textile Institute Student Section
Herman T. Buckley, Chairman; Robert A. Lemieux, Secretary.

North Carolina State College Student Section
J. E. Spainhour, Chairman; J. A. Holder, Secretary.

Philadelphia Textile School Student Section
Wayne F. Fry, Chairman; Robert Roecker, Secretary

Members should notify **Secretary** immediately of all address changes

Quarterly Research Number

NUMBER 4

CONTENTS

Stress-Strain Characteristics of Wool as Related to Its Chemical Constitution P168
J. B. Speakman

Communication Re: Stress-Strain Characteristics of Wool as Related to Its Chemical Constitution P171
Milton Harris and Arnold Sookne

The Reaction of Wool with Hydrogen Peroxide P173
Henry A. Rutherford and Milton Harris

Photochemical Reaction of Wool P175
Milton Harris and Arthur L. Smith

The Detection of Oxidation in Wool P179
Henry A. Rutherford and Milton Harris

Methods of Determining Oil, Soap and Other Extraneous Matter in Textile Materials
III. Investigation of the Nature of the Material Obtained by the Extraction of Commercially Clean Wool with Ethyl Ether P180
Bertil A. Ryberg

Bibliography on the Chemistry of Wool P183
Arthur L. Smith and Milton Harris

AMERICAN DYESTUFF REPORTER
Official Journal

Stress-Strain Characteristics of Wool As Related to Its Chemical Constitution

J. B. SPEAKMAN, D.Sc., F.I.C., F.T.I.*

IN their recent paper[1] under the above title, Sookne and Harris make use, for the first time, of one of the various mechano-chemical methods[2] devised in this laboratory for studying the structure and properties of animal fibers such as wool. Some of these methods have now been in use for about ten years, their utility, convenience and precision have been established, and their adoption by other workers has been awaited with interest. Unfortunately, the first experiments of Sookne and Harris are open to criticism because either the experimental conditions are such as to lead to false conclusions, or the deductions made from sound experiments are false. The purpose of the authors was to show that the salt linkages[3] formed from the acid and basic side chains of wool do not contribute appreciably to the physical stability of the fiber in aqueous solutions; and that the weakening of fibers in acid solution is not due to salt linkage breakdown, but to fiber swelling. In order to refute these contentions, it will be necessary to discuss Sookne and Harris' paper in some detail, even though there is then a danger that the reply may be regarded as a polemic. The purpose of the following discussion is to prevent perpetuation of the erroneous conclusions drawn by Sookne and Harris, and to prevent misuse of the mechano-chemical methods of experiment in the future. For convenience, the paper is discussed under the headings employed by Sookne and Harris.

1. *Effect of Tanning.*

In this connection, Sookne and Harris discuss the strengthening effect of quinone on wool, which was discovered by Meunier[4] in 1911. The reaction has been studied on a number of occasions in this laboratory, and there can be no doubt that wool fibers are strengthened by being boiled in aqueous-alcoholic quinone. Sookne and Harris, however, argue that "In view of the fact that the tanning process has blocked many of the basic groups in wool (as evidenced by the decreased acid-combining capacity) it would be expected from the salt-linkage theory that less energy would be required to elongate the tanned fibers 30 per cent than is required for untreated fibers". Because the fibers are not weakened, they deduce that "the predominant factor affecting the extensibility may be swelling or hydration of the fibers, as will be shown later". Nevertheless, Sookne and Harris admit that the difficulty of stretching quinone-treated fibers may be due to the formation of cross-linkages between the peptide chains, but they state that "there is no evidence in support of such a theory." It is here that Sookne and Harris make their first error: the only reason why no evidence was found is because none was sought. Actually, cross-linkages *are* formed, as can be most simply shown by boiling quinone-treated fibers in 5 per cent sodium bisulfite solution. In conjunction with J. L. Stoves it has been found, for example, that whereas untreated fibers contract 28 per cent under such conditions, quinone-treated fibers contract only 17.7 per cent. Even this difference does not express the full extent of cross-linkage formation, because quinone reacts with the free amino groups in wool, and deaminated fibers contract 50 per cent in boiling 5 per cent sodium bisulfite solution[5]. The presence of these new cross-linkages has been established in other ways by C. E. Coke in this laboratory, giving a precise explanation of the increased resistance to extension of quinone-treated fibers. Sookne and Harris have no reason, therefore, to conclude from experiments with quinone-treated fibers that swelling, and not salt linkage breakdown, is the cause of the reduced resistance to extension of untreated fibers in acid solution. The primary cause is salt linkage breakdown, although a supplementary effect is given by the swelling which succeeds salt linkage breakdown, as has been emphasized in a number of papers from this laboratory[6]. Finally, it must be mentioned that Sookne and Harris' treatment of the action of quinone on wool is entirely superficial: the reaction is complicated, and the formation of new cross-linkages does not take place solely in the manner which would at first sight be expected. A full account of the reaction will be given in another place.

2. *The Effect of Dyeing with Acid Dyes*

In an effort to substantiate the false conclusion that salt linkage breakdown is not the cause of the diminished resistance to extension of untreated fibers in acid solution, Sookne and Harris carried out experiments with fibers dyed with excess of Orange II in 0.1 N hydrochloric acid. The dyed fibers were washed in running water for 1 hour, and allowed to stand in buffer solutions for 24 hours, before the second extension. With Orange II, dye is stripped from the fibers in running water, as well as in the buffer at pH 6.90, so that the fibers, especially in the latter case, can not be regarded as saturated with dye. The point is

*Textile Chemistry Laboratory, Leeds University, England.

unimportant in relation to Sookne and Harris' argument, however, because their main deduction is that since the dyed fibers show the same resistance to extension in hydrochloric acid at pH 1.42 to 4.95, as do untreated fibers in water, salt linkage breakdown can not be a primary cause of reduced resistance to extension. This conclusion is again false, as is the statement that "when completely dyed, the wool and dye appear to form compounds which approach homopolar compounds in their behavior." The true cause of the difficulty encountered in stretching dyed fibers at pH 1.42 is simple mechanical hindrance of extension by the dye molecules, as Sookne and Harris would have discovered if they had studied the recovery of fibers from extension, as well as their resistance to extension. A glance at the structure of the wool molecule will indicate how compact the structure is, and how seriously large dye molecules must interfere with main chain folding and unfolding. Actually, a paper dealing with this aspect of wool chemistry was read before the West Riding Section of the Society of Dyers and Colorists on October 28th (The Influence of Dyes and Dyeing Processes on the Milling, Strength and Wearing Properties of Wool Fabrics—by J. B. Speakman, P. E. King and W. T. Liu), and an abstract of the results may be of interest. The method of experiment was to take dyed and undyed fibers through a cycle of extension and contraction[7] in water at 22.2° C., limiting the extension to 30 per cent. The hysteresis between extension and contraction was expressed as a percentage of the work needed to stretch fibers 30 per cent, and typical results are given below.

Fiber	*% Hysteresis*
Untreated	53.7
Dyed with 50% Solway Green G	80.4
Dyed with 50% Solochrome Black	71.3
Dyed with 30% Solway Blue Black BS	73.8

Not only is the resistance to extension increased, but the power of contraction is reduced, showing that the dye impedes extension and contraction by simple mechanical clogging of the fiber structure. In further proof, the formation and deposition of insoluble compounds in the fiber e.g. the tannic acid-tartar emetic resist, was found to increase the hysteresis and resistance to extension, while decreasing the power of contraction of fibers. The paper to which reference has been made deals with about 100 dyeings, but the preceding abstract is sufficient to show that the true cause of the increased resistance to extension of fibers dyed with Orange II is clogging of the fiber structure with large dye molecules, and that Sookne and Harris' statement that salt linkage breakdown is without effect on the elastic properties of fibers is totally unsupported by their work on dyed fibers.

3. *Effect of Deamination*

In this connection, Sookne and Harris argue that it is difficult to examine the part played by salt linkages in determining the elastic properties of the fiber, from a comparison of untreated and deaminated fibers, because of the difficulty of realizing complete deamination in a reasonable time, and because of the action of nitrous acid on cystine linkages. As regards the former, single fibers can be deaminated completely in two days, and the main difficulty with wool in bulk is simply one of slow diffusion of nitrous acid through the mass of material. Even with wool in bulk, however, it should be mentioned that C. S. Whewell has been able to reduce the maximum acid combining capacity of wool from 80 c.cs. N/1 hydrochloric acid per 100 g. for untreated wool, to 23.0 c.cs. in 4 days' deamination and 9.6 c.cs. in 8 days' deamination. In view of supposed difficulties, however, Sookne and Harris re-examined the behavior of deaminated fibers in solutions at pH 1.1, 4.0, 7.0 and 12.0. The interpretation of these results is wrongly based on a supposed increased reactivity of the oxidized sulfur linkage at pH 4. If Sookne and Harris had made observations at more frequent intervals of pH, with completely deaminated fibers, the true explanation would have been apparent. Such experiments were made in conjunction with E. Stott in 1936, and it was intended to delay publication until the corresponding complete titration curve of deaminated wool had been determined. In view of Sookne and Harris' paper, however, the results of stretching experiments must be published in advance. The general method of experiment was to compare the resistance to extension of completely deaminated fibers in water and in buffer solutions of varying pH at 22.2° C. The results are expressed as a percentage reduction in the resistance to extension, a method which is more simple and direct than the so-called "indices" used by Sookne and Harris.

TABLE 1

pH.	*% Reduction in Work for 30% extension*
1.00	2.0
2.11	1.3
3.07	— 0.7
3.97	— 0.5
5.00	— 0.1
5.55	2.1
5.97	0.6
6.47	6.6
6.83	10.6
7.44	9.4
8.09	9.1
8.67	10.2
9.20	12.0
9.88	10.8
10.45	12.2
11.23	17.8
11.77	36.6

As indicated in Fig. 1, the data are in complete agreement with the salt linkage hypothesis. According to the latter, the free acid and basic side chains of wool are equivalent,

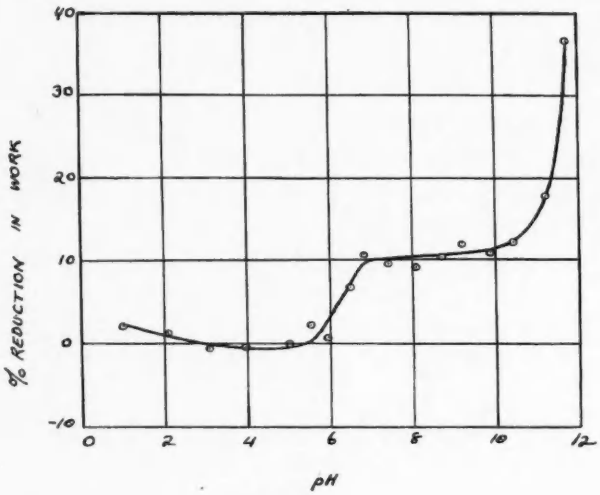


Fig. 1

and the linkages they form oppose extension of the fiber. When the latter is stretched in acid media, extension is facilitated because the salt linkages are broken to an extent depending on the pH. With completely deaminated fibers, on the other hand, the resistance to extension should be sensibly independent of pH in acid media, because the salt linkages are already broken. As shown in Table 1 and Fig. 1, this is actually the case. Sookne and Harris' failure to confirm the result is due simply to the fact that the wool was not fully deaminated, and since the data for deaminated fibers in buffer solutions are referred to the resistance to extension of untreated fibers in water, their results include the effects of variable deamination and attack (if any) on the fibers. Further, according to the salt linkage hypothesis, once the basic side chains of wool are removed by deamination, free acid side chains become available for combination with alkali. They should combine with alkali over a range of pH comparable with that observed in the case of the free carboxylic acid side chains of gelatin. Once more, the results of Table 1 and Fig. 1 are in entire agreement with theory: the reduction in the resistance to extension increases sharply between pH 5 and 7, due to combination of acid side chains with alkali and consequent swelling of the fiber. Further, the resistance to extension remains independent of pH between pH 7 and 10, further reduction taking place when the main peptide chains and sulfur linkages are attacked by alkali. Thus the results obtained with deaminated fibers afford a complete proof of the salt linkage hypothesis, and this conclusion is supported by the form of the titration curve for deaminated wool, which is now nearing completion. Finally, since the resistance to extension of deaminated fibers in solutions below pH 5 is sensibly independent of pH, there can be no doubt that our test[8] for complete deamination is essentially sound, and we may repeat that "A critical test for complete deamination is to be found in the fact that completely deaminated fibers should be no more difficult to stretch in water than in hydrochloric acid at pH 1."

4. *Effect of Neutral Salts*

Finally, in order to obtain further information regarding "the forces involved in the extension of fibers," Sookne and Harris studied the resistance of fibers to extension in solutions of various salts. When the salts were arranged in the order in which they facilitated fiber extension, they were found to be arranged in the order of their ability to increase the swelling of proteins. Actually, it has been shown in a number of papers from this laboratory[6] that reagents which induce swelling do decrease the resistance of fibers to extension, but Sookne and Harris' evidence in favor of the classification of their salts is by no means convincing. They have overlooked the fact that strained cystine linkages are more reactive than unstrained, and that salts which have normally no action on cystine linkages become reactive when the fiber is stretched.[9] For example, C. E. Coke, during the course of a lengthy study of the action of inorganic salts on wool, has been able to show that whereas mercuric chloride has little action on unstrained cystine linkages at 22.2°C., drastic reaction occurs when fibers are stretched in the reagent (0.2M $HgCl_2$ in 0.1 N HCl). The only salts in Sookne and Harris' list which have any significant action in reducing the resistance of fibers to extension are potassium iodide and potassium thiocyanate, both of which are open to criticism as being likely to react with strained cystine linkages during fiber extension.

Sookne and Harris' purpose in conducting experiments with neutral salts was, of course, to show that swelling is a sufficient cause of increased ease of fiber extension without invoking a direct effect due to salt linkage breakdown, even in the case of acid solutions. In the latter case, however, it has been shown that the maximum reduction in the resistance to extension in hydrochloric acid is unaffected by the presence of salt in 0.2N concentration, even though the salt does depress swelling.[6] For this reason, and because fibers, after deamination, show the same reduction in resistance to extension in water, as do untreated fibers in acid solution, it was argued that the primary cause of the increased ease of extension of untreated fibers in acid solution is the breakdown of salt linkages. It was also shown, particularly in the case of concentrated solutions of weak acids, that where salt linkage breakdown is accompanied by intense swelling, the latter also contributes to the ease of extension. Sookne and Harris' effort is to prove that salt linkage breakdown has no direct contribution to make to the ease of extension, but acts indirectly through the swelling which follows salt linkage breakdown. Their final argument in this connection concerns the fact that 0.2N salt, which was used in some of our experiments as indicated above, is insufficient to give complete depression of swelling. Sookne and

Harris therefore proceed to use 0.1N hydrochloric acid saturated with sodium chloride. In doing so, they overlook an important fact, established many years ago in this laboratory,[10] that the behavior of fibers in solutions of inert salts etc. is the behavior of fibers exposed to atmospheres in equilibrium with the solutions. The relative humidity given by a saturated salt solution is, however, only about 75% at 0°C., so that fibers immersed in this reagent and stretched would show a "30% index" of 1.71. In Sookne and Harris' case, when fibers were stretched in the 0.1N hydrochloric acid solution saturated with salt, the observed index was 1.10, so that breakdown of salt linkages in hydrochloric acid reduced the index by the very high figure of 0.61. The only error involved in this calculation is that of assuming hydrochloric acid to have no influence on the vapor pressure of a saturated salt solution, and the error, if corrected for, would merely increase the calculated value of the index. In other words, Sookne and Harris' experiment lends considerable support to the hypothesis they hoped to disprove.

No attempt has been made in the preceding discussion to deal with all the errors in Sookne and Harris' paper, but it is hoped that sufficient has been written to indicate that their experiments with tanned fibers, dyed fibers, deaminated fibers and fibers in neutral salt solutions, do not invalidate the salt linkage hypothesis. In no way does the evidence advanced in their paper justify the conclusion that "salt linkages . . . do not contribute appreciably to the physical stability of the fiber in aqueous solutions." Apart altogether from what has been written in reply to Sookne and Harris' paper, there is much evidence to the contrary in the published papers of this laboratory. Mention need only be made of the fact that salt linkages have been shown to oppose folding of the keratin molecules from the state known as α-keratin to a more compact state[11]; and that, under the correct conditions, the stress residing in the salt linkages of stretched fibers may be great enough to rupture the fiber.[12]

In conclusion, it may perhaps be permissible to use this opportunity to mention an error in one of Harris' earlier papers on the "Reaction of Wool with Strong Solutions of Sulfuric Acid."[13] The author argues that a sulfamic acid is formed when wool reacts with 80% sulfuric acid, but the probability that other side chains, such as that of tyrosine, are sulfonated is completely overlooked. Until the possibility is eliminated, the case for sulfamic acid formation must be regarded as unproved.

REFERENCES

[1]Amer. Dyestuff Reporter, *26*, P659 (1937).
[2]Speakman. J. Text. Inst., *18*, T431 (1927); *24*, T273 (1933); *27*, P233 (1936). J. Soc. Dyers and Colourists, *52*, 341 (1936).
[3]Speakman. Nature, Dec. 26th, 1931; *139*, 411 (1931). Trans. Faraday Soc., *29*, 148 (1933).
[4]J. Soc. Dyers and Colourists, *27*, 214 (1911).
[5]Speakman. J. Text. Inst., *27*, P248 (1936).
[6]Speakman. Proc. Roy. Soc., *132A*, 167 (1931); Trans. Faraday Soc. *29*, 148 (1933); J. Soc. Leather Trades' Chemists, p229 (1933).
[7]Speakman. J. Text. Inst., *24*, T273 (1933).
[8]Speakman. J. Text. Inst., *24*, P169 (1933); Speakman and Stott. J. Soc. Dyers and Colourists, *50*, 341 (1934).
[9]Speakman. J. Soc. Dyers and Colourists, *52*, 423 (1936); J. Text. Inst., *27*, P231 (1936).
[10]Speakman. J. Soc. Chem. Ind., *48*, 321T (1929); Proc. Roy. Soc., *132A*, 167 (1931).
[11]Speakman. J. Soc. Dyers and Colourists, *52*, 335 (1936); J. Text. Inst., *27*, P231 (1936).
[12]Speakman. J. Soc. Dyers and Colourists, *52*, 425 (1936).
[13]Harris, Mease and Rutherford. J. Research NBS. *18*, 343 (1937).

COMMUNICATION

Re: Stress-Strain Characteristics of Wool as Related to Its Chemical Constitution

National Bureau of Standards
Washington

December 23, 1937.

L. A. Olney, Chairman,
Research Committee, A.A.T.C.C.

Dear Sir:

Dr. Speakman's discussion of our recent paper on "Stress-Strain Characteristics of Wool as Related to its Chemical Constitution", in which he offers different interpretations for our experimental results, has been read by Mr. Sookne and myself. In investigations dealing with the chemistry of proteins, considerable speculation is necessarily involved in the interpretation of data, and we fully realize that it is a relatively simple matter for different investigators to arrive at different conclusions from the same data. Unfortunately, Speakman does not appear to have examined our data critically and his interpretations are based on what we consider questionable hypotheses or on hypotheses that in our opinion can be shown to be invalid. It is the purpose of this letter to discuss his criticisms and to show that they have not altered our original interpretation of the data. The points are taken up in the order in which they appear in his discussion.

1. Effect of Tanning—In our original paper, we presented data which indicated that tanning wool with quinone appears to decrease the ease of extension of the fibers (except in strongly alkaline solutions) by decreasing the swelling of wool. Speakman argues that the increased resistance to extension is the result of cross-linkage formation, his argument being based on the contracting powers of the quinone-treated fibers. Since we are not in complete agreement with Speakman's hypothesis as to the chemical mechanism of supercontraction, we feel that such evidence is not conclusive. Cross-linkage formation by the quinone fails to account for the fact that quinone tanned fibers are so readily extended in the more alkaline solutions. The affinity of proteins for quinone is enhanced by alkalies and we have found that very little quinone is removed from the tanned wool during alkaline treatments of the type given. Furthermore, it seems unlikely that the fact that the decrease in extensibility of quinone-tanned fibers between pH 5 and pH 1 is proportional to the de-

crease in acid-combining capacity is the result of a coincidence, especially since Speakman has demonstrated that the reduction in work necessary to elongate a fiber 30 per cent is proportional to the amount of acid combined with the wool.

2. Effect of Dyeing with Acid Dyes—Although a very small amount of dye is stripped from the samples soaked at pH 6.9, those soaked in the more acid solutions lost only a negligible amount and can be shown to be saturated with respect to dye. On the basis of Speakman's assumption that the cause of the difficulty in stretching dyed fibers is simple mechanical hindrance, it would be very difficult to explain why the dyed fibers in solution from pH 1.4 to pH 5 required *exactly* the same amount of energy to be elongated 30 per cent as do the untreated fibers. It would be a strange coincidence if the amount of mechanical hindrance in fibers containing the same amount varied and was just enough in each case to give the same value for fibers elongated in solutions up to pH 5. Also, if mechanical hindrance occurs up to about pH 5, does the low value which we obtained for the dyed fibers elongated in solutions at pH 6.9 indicate that the dye facilitates extensibility at this pH?

Speakman also presents some data for the purpose of showing that the dye also impedes contraction of the fiber. Since he does not state how the dyeings were made, it must be pointed out that valid comparisons of the effect of dyes on wool cannot be made unless the dyeing conditions (especially of temperature) are identical and the dyes are of similar types. The amount of damage produced in wool under the conditions of our experiments is very low whereas it can readily be demonstrated that wool subjected to commercial dyeing processes is appreciably damaged. The argument that the dye impedes extension and contraction by simple mechanical clogging of the fiber is subject to criticism since there does not appear to be a direct relation between the ease of extension and the power to contract. For example, Speakman has shown that although the extensibility of untreated fibers increased with increasing temperature, the percentage hysteresis decreased with increasing temperature up to about 35° C. and then increased with increasing temperature above that point. We have encountered examples of increased hysteresis resulting from treatments which either increase or decrease the ease of extension of the fibers.

3. Deamination—Speakman considers that the wool used in our experiments was not fully deaminated, even though we treated less than 50 fibers with more than 100 ml. of a solution of nitrous acid of the strength used by him and for periods up to about four times as long as he used. Whether or not they were "completely deaminated" may be open to question but they should have been deaminated to the same or a greater extent than those used in Speakman's experiments. The controversial point is the criterion for "complete deamination" and our data show that the ease of extension of deaminated fibers in solutions below pH 5 is *not* independent of pH, as required by Speakman's hypothesis.

Speakman also ignores attack of the nitrous acid on groups other than the amino groups. The large increase in extensibilities of the fibers in the alkaline solutions with increasing duration of deamination must be the result of secondary attack of the nitrous acid on the wool. There is considerable evidence to show that some secondary attack occurs at the disulfide linkages.

4. Effect of neutral salts—Speakman states that the classification of the neutral salts in the order in which they increase the ease of extensibility of wool fibers is not convincing. It would indeed be a coincidence if when the six salts used were arranged in the order of their ability to increase the ease of extension of the fibers, they were also arranged in the order in which they increased the swelling of proteins. The possibility of reaction of potassium iodide and potassium thiocyanate with strained cystine linkages has been suggested. However, fibers stretched in 1 N solutions of the latter, washed, and re-extended in distilled water yielded 30 per cent indices of 0.98, showing practically complete recovery. It is of interest to note that these two salts, in addition to their pronounced effect on the extensibility of the fibers, are by far the most active in peptizing proteins. The effect of mercuric salts on stretched wool cannot be compared with that of corresponding potassium salts since it is well-known that the former, in addition to the salts of other heavy metals such as copper and silver, produce dismutative effects on the disulfide group of cystine.

Speakman predicts that the 30 per cent index of a fiber immersed in a saturated salt solution should be 1.71, although actual experiment shows it to be 1.3. His calculation is based on his hypothesis that the behavior of fibers in solutions of inert salts is the behavior of fibers exposed to atmospheres in equilibrium with the solutions. That this hypothesis is not true is obvious since the relative humidity of the atmosphere in equilibrium with any salt solution is lower than that of the atmosphere in equilibrium with water itself at the same temperature and yet, as we have shown, fibers are more easily extended in some salt solutions than they are in water. A more specific example is obtained by comparing the behavior of fibers in lithium bromide and sodium chloride solution. The relative humidity of the atmosphere in equilibrium with a 5 *N* solution of lithium bromide at 20° C. is about 65 per cent as compared to 78 per cent for that of an atmosphere in equilibrium with 5 *N* solution of sodium chloride at the same temperature. However, the 30 per cent index of fibers stretched in a 5 *N* solution of lithium bromide is only 0.82 whereas that of fibers stretched in a 5 N solution of sodium chloride is 1.22.

Finally, although it has no direct bearing on the paper in discussion, Speakman includes a statement relative to a

previous paper from this laboratory on the reaction of wool with strong solutions of sulfuric acid. The paper is concerned with a phenomenon noted by Mr. Mease of these laboratories; namely, that wool treated with an 80 per cent solution of sulfuric acid gained considerably in weight. An investigation was undertaken to study the nature of the reaction and the properties of its product, and as stated in our paper, the results *suggested* that a sulfamic acid derivative is formed. The possibility of sulfonic acid formation was considered but since very much more drastic conditions are usually necessary to form and also to break down such compounds, it was considered unlikely but not impossible that a sulfonic acid was formed. The authors are making further studies of this reaction but will welcome any demonstration, based upon experimental data, of a different mechanism. Until such evidence is forthcoming, we shall continue to rely on the explanation which we have previously suggested as a working hypothesis.

In conclusion, we feel that our original interpretation of the data in question; namely, that the extensibility of wool fibers in aqueous solutions is governed for the most part by the factors which influence the swelling or hydration of the wool, has not been altered by the criticisms offered. Additional experimental evidence, which is now available, will be presented when time permits.

MILTON HARRIS
ARNOLD SOOKNE

The Reaction of
Wool With Hydrogen Peroxide

HENRY A. RUTHERFORD and MILTON HARRIS*

The reaction of wool with hydrogen peroxide was investigated. The basic groups in wool are unaffected during treatment with hydrogen peroxide, as indicated by the determination of the amino nitrogen, arginine and lysine contents. The percentage of each of the elements in wool with the exception of oxygen decreases with increased oxidation but the ratios of these elements remain constant. The results constitute further evidence that the main reaction of wool with hydrogen peroxide is the addition of oxygen to the disulfide groups.

I. INTRODUCTION

THE effect of hydrogen peroxide on wool, chiefly from the standpoint of the effect on the disulfide group, has been studied extensively by Smith and Harris[1, 2, 3, 4, 5]. The results of the investigations indicate that intermediate oxidation products of the disulfide group of the cystine in wool, similar to those obtained from cystine itself by Toennies and Lavine[6, 7], were formed. The latter workers isolated and studied two of these partially oxidized derivatives of cystine. Because of the liability of these compounds in acid and alkaline solutions, it was impossible to isolate any of them from the hydrolysates of oxidized wool, and as a result, the experimental evidence on which was based the postulation that partially oxidized sulfur compounds are present in oxidized wool, was of an indirect nature.

The present investigation, which is an extension of the earlier work, was undertaken to obtain more direct evidence on the nature of the effect of hydrogen peroxide on wool. The results of studies on the possibilities of oxidation of basic groups in wool are also included.

*Research Associate at the National Bureau of Standards representing the American Association of Textile Chemists and Colorists. This work was aided by a grant from the Textile Foundation, Inc.

II. RESULTS AND DISCUSSION

Data which were presented in connection with a paper[8] on the nature of the acid-dyeing process showed that the acid-combining capacity of wool decreased with increasing degrees of oxidation by hydrogen peroxide. Preliminary analyses of these oxidized samples also indicated that the total nitrogen content decreased with increased oxidation. These results at first suggested that an oxidative deamination was probably the cause of the decreased basicity of the samples. However, analyses of the basic groups and basic amino acids in oxidized wool did not substantiate such a mechanism. Determinations of the amino nitrogen in the different samples by the method of Rutherford, Harris and Smith[9] showed no decrease with increasing amount of oxidation. Furthermore the contents of arginine and lysine in the most highly oxidized sample, as determined by isolation as the flavianate[10] and picrate[11], respectively, were the same as those of a sample of the untreated wool. The complete data are given in table 1.

It is obvious that the basic groups of wool were not appreciably affected by the treatment with hydrogen peroxide, and it was therefore necessary to acount in some other way for the decreases in nitrogen content and acid-

TABLE 1

Effect on Wool of Treatment with a 3 per cent Solution of Hydrogen Peroxide at 50° C. for Different Lengths of Time.

Duration of treatment	*Total nitrogen*	*Acid-combining capacity*	*Amino nitrogen*	*Arginine*	*Lysine*
hrs.	*per cent*	*Milli-equiv. per g. of wool*	*mg/g*	*per cent*	*per cent*
0 (Untreated)	16.37	0.80	3.2	7.1	1.7
3	16.24	.60	3.0		
6	16.16	.53	3.2		
10	15.98	.42	3.2		
15	15.99	.34	3.3		
20	16.04	.32	3.2	7.2	1.9

combining capacity. If it is assumed that oxidation by hydrogen peroxide results in the addition of oxygen to the disulfide groups to form such compounds as R-SO-S-R, R-SO-SO-R, R-SO_2-SO-R etc., then an answer to the apparently conflicting data in table 1 is readily found. The oxidation derivatives of the types shown are relatively strong acids and therefore decrease the amount of acid combined with the wool. Also, if oxygen has been added, there will be an increase in weight accompanied by an apparent decrease in nitrogen content.

In order to determine whether an increase in weight of the sample actually occurred during oxidation, the following experiments were made. Skeins, weighing approximately 5 g. each, were placed in U-tubes and dried to constant weight in a stream of dry nitrogen at 105° C. The skeins were then treated with 200 ml. of a 3 per cent solution of purified hydrogen peroxide at 50° C. for different lengths of time. The hydrogen peroxide used in these experiments was prepared by distillation, under reduced pressure, of a 30 per cent solution of C.P. hydrogen peroxide, the distillate finally being diluted to 3 per cent. The skeins of oxidized wool were finally washed with distilled water until the wash water was free from hydrogen peroxide. The mother liquor and wash waters of each sample were combined and evaporated nearly to dryness on a steam bath. The solutions were then transferred to weighing bottles, evaporated to dryness at about 60° C., and finally dried to constant weight at 105° C. Microscopic examination of the residue indicated that the bulk

TABLE 2

Increase in the Weight of Wool Samples After Oxidation with a 3 per cent Solution of Hydrogen Peroxide at 50° C. for Different Lengths of Time

Duration of treatment hrs.	*Increase in weight per cent*
3	0.28
6	.90
10	1.02
15	1.36
20	1.17

of the material was in the form of fine fibers which had been lost during the treatment. The weights of the residues accounted for only a part of the net increases in the weights of the samples. The weights of the dry residues were added to the weights of the corresponding oxidized samples, which had been dried at 105° C. in a stream of dry nitrogen. The increases in weight shown in table 2, are very appreciable, and account for a large portion of the apparent decrease in nitrogen contents shown in table 1.

If the principal effect of this type of oxidation of wool is the addition of oxygen to the disulfide groups, then the percentage of each of the elements except oxygen in wool should decrease with increased oxidation, but the ratios of these elements in any sample should be constant. Analyses given in table 3 for the carbon, hydrogen, nitrogen, and sulfur in untreated samples and in samples oxidized for 10 and for 20 hours by the procedure previously described, show that this is so. The results constitute further evidence that the main reaction of wool with hydrogen peroxide is the addition of oxygen to the disulfide groups.

III. REFERENCES

[1]J. Research NBS *16*, 301 (1936) RP875.
[2]J. Research NBS *16*, 309 (1936) RP876.
[3]J. Research NBS *17*, 97 (1936) RP904.
[4]J. Research NBS *17*, 577 (1936) RP928.
[5]J. Research NBS *18*, 623 (1937) RP998.
[6]J. Biol, Chem. *113*, 571 (1936).
[7]Personal Communication.
[8]J. Research NBS *19*, 81 (1937) RP1012.
[9]J. Research NBS *19*, 467 (1937) RP1038.
[10]J. Biol. Chem. *106*, 457 (1934).
[11]J. Biol. Chem. *109*, 703 (1935).

TABLE 3

Elementary Analysis of Untreated Samples of Wool and of Samples which had been Treated with a 3 per cent Solution of Hydrogen Peroxide at 50° C. for 10 and for 20 Hours

Duration of treatment hrs.	*Carbon per cent*	*Hydrogen per cent*	*Nitrogen per cent*	*Sulfur per cent*	*Oxygen (by difference) per cent*	*Ratio* C	H	N	S
0 (Untreated)	50.04	6.92	16.37	3.58	23.09	1	0.138	0.328	0.071
10	49.72	6.83	15.98	3.45	24.02	1	0.137	0.322	0.069
20	49.15	6.80	16.04	3.39	24.61	1	0.138	0.326	0.069

Photochemical Reaction of Wool*

MILTON HARRIS and ARTHUR L. SMITH†

In an earlier paper, the authors suggested that in the photochemical deterioration of wool, a portion of the sulfur is converted to hydrogen sulfide, some of which is subsequently oxidized to sulfuric acid. The present paper describes an apparatus which was developed for the purpose of segregating these reactions and testing the above hypothesis. The results obtained with it show that in an atmosphere of purified nitrogen, hydrogen sulfide is evolved from wool during irradiation. In the presence of air the bulk of the hydrogen sulfide is oxidized to sulfuric acid. The rate of evolution of hydrogen sulfide is increased by the presence of moisture. The data suggested that the primary action of the radiation is an activation of the disulfide group, resulting in a change in the state of the sulfur. A secondard process, involving the evolution of hydrogen sulfide from the irradiated wool then occurs. Water does not appear to be essential to the process which involves changing the state of the sulfur but may play an important part in the secondary reactions.

I. INTRODUCTION

In an earlier paper[1], on the effect of light on wool, the authors suggested that the result of irradiation is the conversion of a portion of the sulfur to hydrogen sulfide, some of which is subsequently oxidized to sulfuric acid. In order to test this hypothesis, it was necessary to devise experiments which would segregate those reactions. The present paper describes an apparatus which was developed for this purpose. The results obtained with it are used to further elucidate the nature of some of the photochemical reactions in wool.

II. DESCRIPTION OF APPARATUS AND TECHNIQUE OF OPERATION

A schematic diagram of the apparatus for exposing the wool under controlled atmospheric conditions, to the radiation of a glass-enclosed carbon arc** is shown in figure 1. Gases which may be evolved from the fibers are removed by carrier gases and absorbed by suitable reagents. During an exposure of a sample, the carrier gas is introduced at A and passes over the mercury safety valve B, through the trap C, and then through the absorption towers D and E. The latter have a capacity of about 800 ml. each and are equipped with platinum disks for distributing gas similar to those described by Shepherd[2] for gas absorption pipettes. The disks are perforated plates, each 0.05 mm. thick and 20 mm. in diameter, and with 212 evenly spaced holes, 0.06 mm. in diameter. When nitrogen is used as the carrier gas, D and E are filled with an alkaline solution of pyrogallol. These towers do not need to be filled when air is used. However, it was found that the presence of liquid in them facilitates the regulation of the flow of the gas. Furthermore, if a saturated solution of potassium hydroxide is used in the second tower E, the air is partially dried, thus permitting the material in the drying tower J to be used for a longer period of time. After the gas leaves E, it is divided into two portions, the relative amounts of each being regulated by stopcocks F and G. Part of the gas passes through H, which is filled with distilled water, and the remainder is dried by passing through J, which is filled with anhydrous magnesium perchlorate.‡ From them the gas passes through the exposure tubes K and L, which contain the wool samples.

The gas emerging from each of the tubes K and L, finally passes through two small absorption towers MN and OP, in series. These towers have a capacity of 250 ml. each and are constructed the same as the larger ones, D and E. In addition they are fitted with ground glass stoppers on the intake tubes to facilitate washing of the inside of the platinum distributors. Since each gas was determined in a separate experiment the towers MN and OP were filled with the same solution. The solutions were as follows: 0.1 N solution of hydrochloric acid for the absorption of am-

‡It was shown that when 210 liters of air, saturated with moisture, was dried by passing over anhydrous magnesium perchlorate at 25° C. at the rate of from 1.5 to 3.5 liters per hour, the residual air did not contain a weighable amount of water[9].

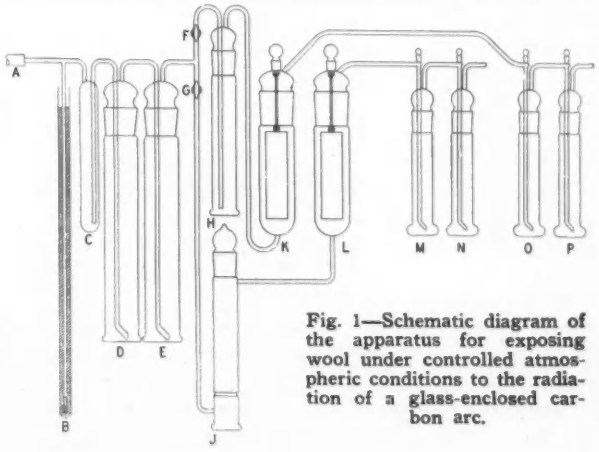


Fig. 1—Schematic diagram of the apparatus for exposing wool under controlled atmospheric conditions to the radiation of a glass-enclosed carbon arc.

*Publication Approved by the Director of the National Bureau of Standards of the U. S. Department of Commerce.

†Research associates at the National Bureau of Standards representing the American Association of Textile Chemists and Colorists. This work was aided by grants from the Textile Foundation, Inc., and the Eavenson Levering Company. Present address of Arthur L. Smith is Eavenson Levering Company, Camden, New Jersey.

**Fade-Ometer, Atlas Electric Devices Co., Chicago, Ill.

monia; a solution containing ten grams of sodium hydroxide and ten grams of bromine per liter for the absorption of hydrogen sulfide; and a 15 per cent solution of cadmium chloride for determining whether the evolved gas was hydrogen sulfide or sulfur dioxide.

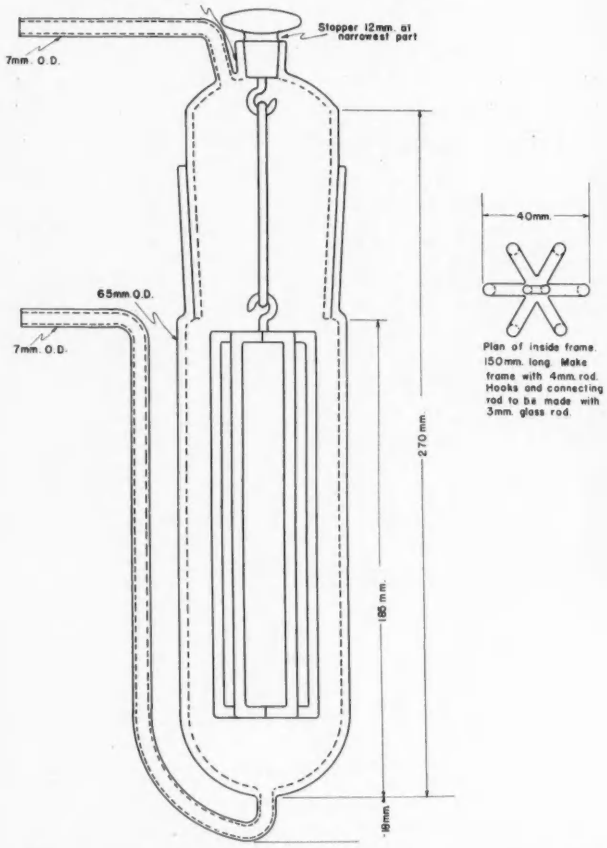

Stopper 12mm. at narrowest part
7mm. O.D.
65mm O.D.
7mm. O.D.
40mm.
Plan of inside frame. 150mm. long. Make frame with 4mm. rod. Hooks and connecting rod to be made with 3mm. glass rod.
270 mm.
185 mm.
19mm.

Fig. 2—Detailed drawing of the hexagonal glass framework on which the wool is mounted, and of the tube in which the wool is exposed.

Figure 2 is a detailed drawing of the exposure tubes, K and L. Single-ply wool yarn* of very low twist was wound on the hexagonal glass framework. The ground glass stopper, from which the frame is suspended, permits the frame to be revolved at frequent intervals which assures fairly uniform exposures. Difficulties encountered in using ordinary lubricants in the large ground-glass joint, were overcome by using a glycol-phthalic anhydride resin[3].

The complete assembly is shown in Figure 3. The exposure tubes are 10 inches from the carbon arc. A fan, regulated by a bimetallic thermostat, is mounted below the exposure tubes and maintains the surrounding air at a temperature of about 35° C. The temperature inside the

*The yarn was prepared from raw wool which had been extracted with Stoddard solvent and washed with water. It was further purified by extraction in a Soxhlet apparatus with alcohol and ether, for 6 hours, with each, and finally washed with water at 50° C.

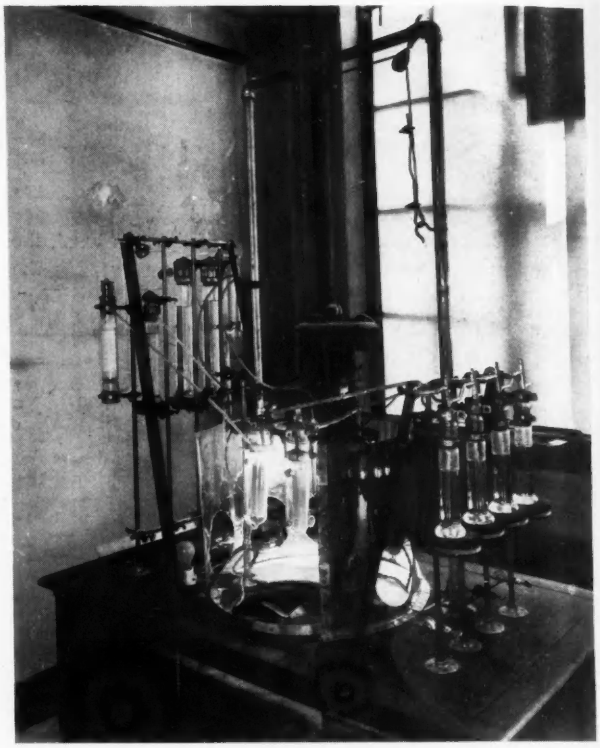


Fig. 3—Complete assembly of the apparatus for exposing wool under controlled atmospheric conditions to the radiation of a glass-enclosed carbon arc. The front section of the aluminum shield has been removed to show the exposure tubes.

tubes, as measured by mercury thermometers, averaged about 60° C. An elliptical aluminum reflector is placed around the lamp and the exposure tubes to increase the intensity of radiation on the samples.

The flow of gas was regulated, during operation, by stopcocks F and G. 300 to 400 ml. of gas per hour was passed over the wool.

III. EXPERIMENTAL RESULTS

When a solution of cadmium chloride was used in absorption towers MN and OP, (Fig. 1) it was found that cadmium sulfide precipitated on the platinum disks, and after about 75 hours, the flow of gas was completely stopped. As a result, some preliminary experiments were made by exposing wool in sealed glass tubes filled with moist and dry nitrogen to the radiation of a glass-enclosed carbon arc which did not have an aluminum reflector around it. The distance of the arc from the tubes was about 10 inches. After 575 hours' exposure, the tubes were opened and the gaseous contents driven out with nitrogen into suspensions of cadmium carbonate. The gas from the tube which was filled with moist nitrogen produced a yellow precipitate in the cadmium carbonate suspensions, which indicated the presence of hydrogen sulfide. A significant amount of yellowing did not occur in the

solution which received the gas from the tube containing wool and dry nitrogen.* The precipitate in the first solution was filtered off and taken up in a dilute solution of hydrochloric acid. The hydrogen sulfide which was liberated was determined by titration with a standard solution of iodine. By this procedure, 5.4 per cent of the total sulfur of the wool was accounted for as hydrogen sulfide. Direct analysis of the sample irradiated in the atmosphere of moist nitrogen showed that 6 per cent of the sulfur was evolved. These results indicate that the bulk of the sulfur is evolved from wool during irradiation in the form of hydrogen sulfide and not as sulfur dioxide† as suggested by King[4] and by Meunier and Rey[5].

The rate at which hydrogen sulfide was evolved during irradiation in nitrogen was determined. The wool was wound on the hexagonal glass frames and dried at 105° C. for 6 hours, after which it was rapidly transferred to the tubes K and L. The latter were covered with black paper, the light was turned on, and dry nitrogen passed over one sample and moist nitrogen over the other for 18 hours. The paper was then removed and the exposures were started. The absorption pipettes MN and OP contained the alkaline bromine solution and any sulfide sulfur evolved was immediately oxidized to sulfate. At various intervals these solutions were removed and the amount of sulfate was determined as barium sulfate. The rates at which sulfur, in the form of hydrogen sulfide, is evolved from the wool are shown in Figure 4.

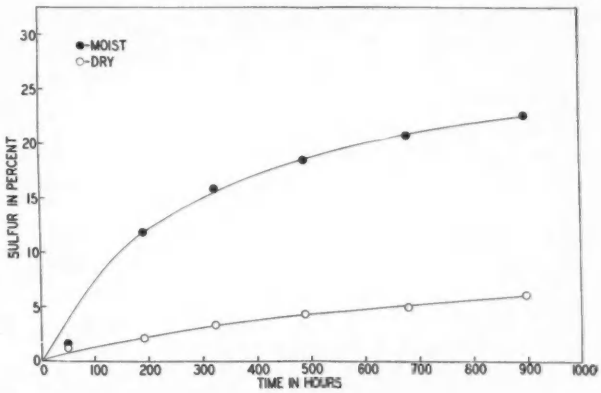


Fig. 4—Rate of evolution of hydrogen sulfide from samples of wool exposed in atmospheres of moist and dry nitrogen to the radiation of a glass-enclosed carbon arc. The ordinate values are in terms of the percentage of the total sulfur which was evolved as hydrogen sulfide during the irradiation.

After 900 hours' exposure, the wool yarn was removed, cut into lengths about one-eighth inch long, and thoroughly mixed to assure uniform sampling. Analyses made on the different samples are shown in table 1.

A similar exposure, using a 0.1 *N* solution of hydrochloric acid in tubes MN and OP showed that in 305 hours' exposure, no appreciable amount of ammonia was evolved from either sample.

A third series of exposures of wool in atmospheres of moist and dry air were made. Under these conditions, relatively little hydrogen sulfide was found. The effect of 266 hours' exposure is shown in table 2.

IV. DISCUSSION

The available data can hardly be considered to be sufficient for a detailed explanation of the photochemical de-

*A comparison of the amount of sulfur lost from the sample irradiated in an atmosphere of moist nitrogen under these conditions with that lost by a sample under similar conditions irradiated in the new apparatus described in this paper indicates that the intensity of the radiation is greatly increased by the aluminum reflector.

†If any sulfur dioxide were present, it would react with hydrogen sulfide as follows:

$$SO_2 + 2H_2S \rightarrow 2H_2O + 3S$$

TABLE 1

Effect on Wool of 900 Hours' Exposure in Atmospheres of Moist and Dry Nitrogen to the Radiation From a Glass-enclosed Carbon Arc

Sample	*Total nitrogen*	*Ammonia nitrogen*	*Cystine*	*Total sulfur*	*Sulfur found in gases*	*Total sulfur accounted for*	*Alkali solubility*	*Sulfur as sulfuric acid*
	per cent	*mg/g*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Unexposed	16.22	0.5	10.7	3.41	....	100.0	15.9	None
Exposed in dry nitrogen.	16.17	0.7	4.2	3.17	0.22	97.2	31.8	None
Exposed in moist nitrogen	16.26	0.6	2.9	2.42	0.79	92.0*	36.9	None

* It was subsequently shown that some hydrogen sulfide was adsorbed on the walls of tube K through which moist nitrogen was passed.

TABLE 2

Effect of Wool of 266 Hours' Exposure in Atmospheres of Moist and Dry Air to the Radiation of a glass-enclosed Carbon Arc

Sample	*Total nitrogen*	*Ammonia nitrogen*	*Cystine*	*Total sulfur*	*Sulfur found in gases*	*Total sulfur accounted for*	*Alkali solubility*	*Sulfur as sulfuric acid (on wool)*
	per cent	*mg/g*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Original sample	16.22	0.5	10.7	3.49	...	100.0	15.9	....
Exposed in dry air	15.87	1.7	5.3	3.16	.06	94.5*	74.5	0.41
Exposed in moist air...	15.81	1.4	5.5	3.00	.05	89.5*	75.7	0.39

* Tests showed that sulfuric acid was adsorbed on the walls of the tubes K and L.

composition of wool. The results of the investigation, however, suggest several generalizations which appear to be useful in further elucidating the nature of some of these reactions.

It is evident from the curves in Figure 4 that the evolution of hydrogen sulfide from wool which was irradiated in an atmosphere of nitrogen was greatly accelerated by the presence of moisture. It would appear at first sight, that a hydrolytic cleavage of the disulfide group of the cystine in wool occurred, similar to the one postulated by Crowder and Harris[6] to account for the degradation of wool in alkaline solutions. Hydrogen sulfide would then be formed according to the following reactions:

$$\begin{array}{l} -CH_2-S-S-CH_2- + H_2O \rightleftharpoons \\ \qquad\qquad -CH_2SH + -CH_2SOH \\ \qquad\qquad\qquad\qquad \downarrow \qquad (1) \\ \qquad\qquad\qquad\qquad -CHO + H_2S \end{array}$$

Assuming the above mechanism, it could be argued that in view of the great difficulty in obtaining absolutely dry wool, it is questionable whether all of the moisture was removed from the so-called dry sample at the start of these experiments. In other words, it would be difficult to tell whether the hydrogen sulfide obtained from the sample exposed in the atmosphere of dry nitrogen resulted from the decomposition of absolutely dry wool, or whether it was influenced by moisture which may still have been present.

If the photochemical decomposition of wool primarily involves a hydrolytic cleavage of the disulfide group, it must be pointed out, that of any moisture remaining on the fibers, some might be used up in photochemical reactions in the early stages of the exposure, but the rest would be rapidly removed by the warm, dry nitrogen which was continually passing over the sample. Under such conditions, there would be anticipated an initial, relatively rapid evolution of hydrogen sulfide, but the rate would soon decrease until practically no further evolution of gas occurred. That this is not so is indicated by the lower curve in Figure 4.

If the decomposition proceeded according to equation 1, it would also be expected that the decrease in cystine content would increase with increasing alkalinity of the sample since the sulfenic acid group (—SOH) becomes increasingly unstable with increasing pH. That the reverse of this actually occurs was demonstrated by the authors in their earlier investigations[1] in which it was shown that the cystine content of a sample of wool treated with 0.1 *N* hydrochloric acid and irradiated 100 hours decreased 52 per cent, whereas that of a sample treated with a 0.1 *N* solution of sodium carbonate and exposed for the same time decreased only 35 per cent.

Finally, it is evident from the data in table 1 that although the moist sample lost more than four times as much sulfur as the dry sample, the cystine content of the former is only slightly lower than that of the latter. A large portion of the cystine is destroyed during the irradiation and if it is assumed that the destruction involves a hydrolytic cleavage of the disulfide group, it is readily seen that an appreciable amount of water would also have had to be present in the dry sample.

It seems more likely that the action of the radiation on wool in an atmosphere of nitrogen *primarily* does not result in hydrolysis of the disulfide group. The data in table 1 show that the cystine contents, as determined by the highly specific Sullivan method[7], decreased about the same amount for the samples exposed in atmospheres of dry or of moist nitrogen, but the moist sample evolved four times as much hydrogen sulfide as the dry sample. This suggests that the primary action is probably an activation of the disulfide group, resulting in a change in the state of the sulfur and a corresponding lowering of the cystine content. A secondary process, involving the evolution of hydrogen sulfide from the irradiated wool then occurs.

The role of the water is of considerable interest. Although water does not appear to be essential to the process, which involves changing the state of the sulfur, it may play an important part in the secondary reaction. That it might conceivably catalyze the secondary reaction, or actually react with products of the primary reaction to liberate hydrogen sulfide, was demonstrated by immersing samples of irradiated wool in warm water. Considerable hydrogen sulfide was evolved, but under similar conditions, a significant amount of hydrogen sulfide was not obtained from untreated wool.

The photochemical reactions which occur when wool is irradiated in atmospheres of moist and dry air are even more complex. In addition to the attack on the sulfur, nitrogen groups are affected, as shown in table 2. The increase in ammonia nitrogen content results from photo-oxidation processes[8]. Only a relatively small amount of hydrogen sulfide is evolved, the bulk of it being immediately oxidized to sulfuric acid. The acid thus formed further catalyzes the photochemical decomposition[1] which accounts for the high alkali-solubilities. The moist sample lost more sulfur, but again the cystine contents and the alkali-solubilities of both the moist and dry sample were changed about the same amount.

V. REFERENCES

[1]J. Research NBS *17*, 97 (1936) RP904; Am. Dyestuff Rept. *25*, p383 (1936).

[2]B. S. J. Research *4*, 747 (1930) RP177.

[3]Physics *1*, 352 (1931).

[4]J. Soc. Dyers Colourists *44*, 14, 233 (1928).

[5]Compt. Rend. *183*, 596 (1926).

[6]J. Research NBS *16*, 475 (1936) RP885; Am. Dyestuff Reptr. *25*, p264 (1936).

[7]Public Health Reports 86 (1930).

[8]J. Research NBS *13*, 151 (1934) RP697; Am. Dyestuff Reptr. *23*, 403 (1934).

[9]J. Am. Chem. Soc. *44*, 2255 (1922).

The Detection of Oxidation in Wool

HENRY A. RUTHERFORD and MILTON HARRIS*

A rapid and simple test for detection of oxidation in wool is described. The method utilizes the oxidizing value of some of the intermediate oxidation derivatives of the disulfide groups in wool, and is based on the ability of oxidized wool to convert a ferrous salt into ferric salt. The latter in the presence of thiocyanate gives the characteristic red color offerric thiocyanate.

I. INTRODUCTION

THE susceptibility of wool to deterioration during wet treatments, especially with alkaline reagents, is appreciably increased if the wool has previously been oxidized.[1] Damage, resulting from oxidation may be produced during bleaching processes, during processes such as chlorination and bromination for producing unshrinkable finishes, and in aging conditions involving exposure to strong light, air, and moisture. Often such damage is not detectable by ordinary physical testing methods. It may, however, be accentuated during the subsequent processing of the fiber. In addition, it has been shown to affect the dyeing properties of the fiber[2] and the durability of woolen materials[3]. The detection of oxidation in wool is therefore of considerable importance.

Two tests for oxidized wool, the alkali-solubility[3] and the lead acetate tests[4], have been suggested by Smith and Harris. The former, although somewhat time-consuming, has the advantage of giving values which have some quantitative significance and it can be used as a control method in practical wool processes. The latter is a qualitative test and more rapid, but fails if the wool has been exposed to light of great intensity.

More recent investigations have indicated that the oxidizing value of some of the intermediate oxidation products of the disulfide groups in wool can be utilized as a test for the detection of oxidation. One method based on this fact depends on the ability of oxidized wool to liberate iodine from hydrochloric acid-potassium iodine solutions[5]. The iodine is determined by direct titration with sodium thiosulfate, but the values have no quantitative significance with respect to the extent of oxidation since only sulfur that is oxidized below the sulfonic acid state is reduced. The method was found to be impractical as a mill laboratory test since the reducing solution is unstable, the reductions must be done in the dark at a constant temperature, and the titrations are difficult because some of the liberated iodine is absorbed by the wool.

A more satisfactory test, which is described in this report, utilizes the ability of oxidized wool to convert a ferrous salt to a ferric salt, which in the presence of a thiocyanate gives the characteristic red color of ferric thiocyanate. Although the test is a qualitative one, it has the advantages of being rapid and simple, and of giving a positive test for wool which has been oxidized by photochemical reactions.

II. DESCRIPTION OF TEST

The following three solutions are required for the test:

1. Solution A consists of equal parts by volume of acetone (reagent-grade) and distilled water, acidified by the addition of 1 per cent by volume of a 6 *N* solution of sulfuric acid. The acetone inhibits dissociation of the ferric thiocyanate and helps to preserve the color[6, 7].

2. Solution B is prepared by dissolving about 1 g. of potassium thiocyanate in 30 ml. of solution A.

3. Solution C is prepared by dissolving about 1 g. of ferrous ammonium sulfate (reagent-grade) in a solution containing 50 ml. of solution A and 15 ml. of 6 *N* solution of sulfuric acid. Solution C must be prepared immediately before the test is made, since some of the ferrous salt is oxidized by air. The best results are obtained if the solution is prepared in an atmosphere of carbon dioxide or nitrogen.

About 1 g. of wool is cut in small pieces and placed in a 125-ml. Erlenmeyer flask containing 40 ml. of solution A and 5 ml. of solution B. The solution is boiled for several minutes to insure displacement of the air in the flask by water and acetone vapors. As soon as the heating is discontinued, 5 ml. of solution C is added and the flask immediately stoppered. For controls, similar tests are made at the same time on a sample of wool known to be unoxidized and on the reagents in the absence of wool. A recommended procedure is to heat all of the test solutions on a hot plate at the same time.

A pink color may develop in the control solution containing only the reagents, and thus decrease the sensitivity of the test. This is overcome by the addition of a measured amount of distilled water until the color just disappears. An equal volume of water is then added to the other test solutions. Under these conditions, unoxidized wool produces no color, while oxidized wool will give various shades of pink depending upon the degree of oxidization of the sample.

The development of a pink color in the test solution

* Research Associates at the National Bureau of Standards representing the American Association of Textile Chemists and Colorists. This work was aided by a grant from the Textile Foundation, Inc.

prior to the addition of solution C indicates the presence of iron in the wool. In such a case, the wool must first be washed with a sufficient number of changes of a very dilute solution of sulfuric acid in distilled water to remove all of the iron.

III. RESULTS

The method as described gave positive tests for wool bleached with hydrogen peroxide, for chlorinated and brominated wool, and for wool which had been exposed in the presence of air and moisture to the radiation of a glass-enclosed carbon arc lamp. Negative tests were obtained for samples of wool irradiated in atmospheres of moist or dry nitrogen and in very dry air. Samples of wool which had been bleached with hydrogen peroxide and subsequently treated with sulfurous acid also gave negative results.

Like the reduction method, using the hydrochloric acid-potassium iodine solutions, the method should have no quantitative significance. Further evidence of this was obtained when it was found that a sample of wool which had been bleached for two hours with a solution of 0.6 per cent of hydrogen peroxide produced a deeper pink color in the test than was produced by a sample of wool bleached with a 1.7 per cent solution for the same length of time. In other words, the latter solution oxidized a greater number of disulfide groups to states of oxidation which resisted reduction. That the method has practical application as a qualitative test, however, is indicated by the fact that a positive test was obtained even with wool which was oxidized with a 3 per cent solution of hydrogen peroxide for 24 hours. Such a treatment is far more drastic than any encountered in wool processing, yet not all of the disulfide groups were oxidized to a stage at which they resisted reduction.

IV. REFERENCES

[1]J. Research NBS *16*, 301 (1936) RP 875; Am. Dyestuff Rept. *25*, P180 (1936).
[2]J. Research NBS *19*, 81 (1937) RP 1012; Am. Dyestuff Reptr. *26*, P416 (1937).
[3]J. Research NBS *17*, 577 (1936) RP 928; Am. Dyestuff Reptr. *25*, P542 (1936).
[4]J. Research NBS *16*, 309 (1936) RP 876; Am. Dyestuff Reptr. *25*, P183 (1936).
[5]J. Research NBS *18*, 623 (1937) RP 998; Am. Dyestuff Reptr. *26*, P413 (1937).
[6]Ind. Eng. Chem., Anal. Ed. *9*, 453 (1937).
[7]J. Biol. Chem. *1*, 451 (1906).

Methods of Determining Oil, Soap and Other Extraneous Matter in Textile Materials*

Project 9-37

III–Investigation of the Nature of the Material Obtained by the Extraction of Commercially Clean Wool with Ethyl Ether

BERTIL A. RYBERG†

INTRODUCTION

THE accepted method today for determining residual wool grease and added oil in wool, consists of an extraction of the wool with any one of three solvents, namely ethyl ether, petroleum ether or carbon tetrachloride. Ethyl ether is generally considered to be the most accurate; however, circumstances force the use of carbon tetrachloride in a great many cases.[1] A difference of opinion exists as to the relative merits of each solvent, but it is not our purpose to determine which is the best.

In the usual method the wool is extracted in a Soxhlet, the solvent removed by evaporation, and the residue dried and weighed. This residue is called oil and grease. To our knowledge, this material has never been thoroughly investigated and its composition definitely established, as it is taken for granted that it is composed of residual wool grease, oil added during processing, and any fatty acids accumulated from scouring.

It is our purpose to investigate this ether extractable material obtained from commercially clean wool and determine its approximate composition, thus indicating the efficiency of the scouring process in removing grease and added oils.

*This project is supported by a grant from the Textile Foundation to the American Association of Textile Chemists and Colorists.

†Research Associate of the American Association of Textile Chemists & Colorists, working at the Lowell Textile Institute, under the direction of the Sub-Committee on Methods of Determining Oil, Soap and Other Extraneous Matter in Textile Materials, Hugh Christison, Chairman. Leslie Christison, John Dalton, Alex. Morrison, Roland E. Derby, Harold W. Leitch, Clarence L. Nutting, Louis A. Olney, John H. Skinkle.

MATERIALS

Two lots of fine Australian wool in top form were obtained, having been prepared in the following manner:—

Lot 1. Wool cleaned from grease by the Solvent process, rinsed in warm water, carded and dry combed. This lot was prepared without using any oil, soap or alkali during processing, other than those naturally present in virgin wool.

Lot 2. This lot was prepared by the conventional method of scouring, using a Red Oil Soda soap and sodium carbonate. It was carded, then backwashed with a sulfated alcohol and dry combed.

These two lots of wool therefore, are representative of the two general methods used for cleaning wool. This incidentally, is the same wool as was used in our previous work as reported in the AMERICAN DYESTUFF REPORTER 27, P8 (1938).

Ethyl Ether, Anhydrous Analytical Reagent complying with the A.C.S. Specifications and containing not over 0.02 per cent of alcohol.

METHODS

The methods used in this work are modifications of existing methods, these modifications having been made in order to adapt them to the nature of the material being investigated.

The wool in top form, was extracted twelve times in a large scale Soxhlet extractor[2] and the ether removed by evaporation. Lot 1 yielded 0.66 per cent of ether extractable material and Lot 2 0.84 per cent based on over dry material.

ANALYTICAL WORK

Determination 1

Free Acids

Duplicate samples of the ether extract were taken up in 50 ml. portions of neutralized 95 per cent ethyl alcohol, three to four drops of phenolphthalein were added and the whole brought to boil. This alcoholic solution was then titrated with 0.1 N alcoholic potash until a pink color permanent for one minute was obtained.

Results	Lot 1	Lot 2
Free Acids as Oleic	22.0%	22.3%

2

Total Ether Solubles After Acidification

Samples of the material being investigated, were neutralized using phenolphthalein and alcoholic potash, then evaporated to dryness. They were taken up in hot water and allowed to digest until the oily material appeared to be fairly well emulsified. The material was transferred to a separatory funnel and an excess of hydrochloric acid was added. The whole was shaken up, then allowed to stand until it had cleared somewhat and also cooled. Ethyl ether was added and the whole shaken. The removal of the fatty materials from the solution was accomplished in the usual manner by treatments with ether. The ether portion was then thoroughly washed with water until neutral, filtered, evaporated, dried and weighed.

Results	Lot 1	Lot 2
Ether Solubles after Acidification	98.3%	96.6%

3

Total Ether Soluble Acids

The ether soluble materials from determination two was taken up in 50 ml. of neutralized 95 per cent alcohol and phenolphthalein was added. The whole was brought to a boil and then titrated with 0.1 N alcoholic potash until the pink color obtained is permanent for one minute.

Results	Lot 1	Lot 2
Ether Soluble Acids as Oleic	22.1%	24.4%

4

Combined Acids

Combined acids (fatty) are usually found by determining the total acids and the free acids, the difference being combined acids.

Results	Lot 1	Lot 2
Combined Acids as Oleic	0.0%	2.1%

5

Water Soluble Acids

The aqueous portion remaining after determination two was retained and enough alcoholic potash added to exactly neutralize the standard acid previously added. This solution was then carefully evaporated to dryness on the water bath, then extracted thoroughly with several portions of boiling alcohol. Phenolphthalein was added to the alcoholic solution and the whole titrated with standard alcoholic potash. The neutralized solution was evaporated to dryness on the water bath and weighed. The added alkali was subtracted and the acid calculated to an equivalent weight of 254.[3]

Results	Lot 1	Lot 2
Water Soluble Acid (254) Gravimetric	1.86%	2.01%
Volumetric	1.83	1.94

6

Unsaponifiable Matter

Samples of the extract being investigated were placed in conical flasks, alcoholic potash added and the whole digested under a reflux for several hours. The material was transferred to a casserole and neutralized with sodium bicarbonate, then evaporated nearly to dryness. At this point a small amount of previously extracted sand was stirred in, and the drying carried on to completion. The sandy mass was then transferred to an extraction thimble which was in turn placed in a Soxhlet extractor. This material was extracted for six hours with ethyl ether, the ether portion then being filtered, evaporated to dryness and weighed.

Results	Lot 1	Lot 2
Unsaponifiable Matter	32.3%	34.2%

7

Total Ether Soluble Acids After Removal of the Unsaponifiables

The sandy mass or residue from the determination of unsaponifiables was carefully leached with several portions of hot distilled water, hydrochloric acid was added in excess and the whole was digested on the water bath for one hour. The solution was carefully transferred to a separatory funnel, cooled and extracted three times with ethyl ether. The combined ether portions were washed thoroughly with distilled water, then filtered, evaporated and dried on the water bath.

The fatty residue from above was taken up in boiling neutral alcohol, phenolphthalein added and titrated with alcoholic potash.

Results	Lot 1	Lot 2
Total Fatty Acids—Gravimetric	66.0%	64.2%
As Oleic—Volumetric	57.0	55.5

The increase in total fatty acids after a thorough saponification and removal of the unsaponifiables, indicates the presence of a considerable amount of esters, probably esters of the higher alcohols or sterols. The large discrepancy between the gravimetric and volumetric results indicates that the fatty acids present in this ether extractable material, are of a somewhat higher equivalent weight than oleic acid. Knowing the weight of these total fatty acids and the amount of alkali necessary to neutralize them, it was possible to calculate their equivalent weight which proved to be 326. This figure checks very well with the work of Lewkowitsch[4] on wool grease, he having found a mean molecular weight of 327.5 for the mixed fatty acids obtained from wool grease. This indicates that the ether extract from commercially clean wool, prepared by either process, is essentially residual wool grease, at least in the case of the wool used in our work.

8

Combined Fatty Acids as Esters

Fatty acids combined as esters are found by difference, that is the difference between total fatty acids after removal of the unsaponifiable matter and total fatty acids under determination three (3).

Results	Lot 1	Lot 2
Total Acids from 7	66.0%	64.2%
Total Acids from 3 calculated to 327.5	25.6	28.3
Fatty Acids as Esters (327.5)	40.4%	35.9%

9

Combined Fatty Acids as Soap

In the case of the solvent processed wool, there appears to be no combined acid as soap, since all of the fatty acids found exist in the free state or as esters of the higher alcohols.

Soap scoured wool shows a small amount of fatty acids combined as soap.

Tabulated Results

		Lot 1	Lot 2
1.	Free Acids as Oleic	22.0%	22.3%
	Free Acids as Equivalent Weight 327.5	25.5	25.8
2.	Total Ether Solubles after Acidification	98.3	96.6
3.	Total Ether Soluble Acids as Oleic	22.1	24.4
	Total Ether Soluble Acids as 327.5	25.6	28.3
4.	Combined Acids as Soap (Oleic)	0.1	2.1
	Combined Acids as Soap (327.5)	0.1	2.4
5.	Water Soluble Acids of Equivalent Weight 254 Grav.	1.9	2.0
	Vol.	1.8	1.9
6.	Unsaponifiable Matter (Gravimetric)	32.3	34.2
7.	Total Ether Soluble Acids after Removal of the Unsaponifiable Matter Grav.	66.0	64.2
	(327.5) Vol.	65.7	64.0
8.	Ether Soluble Acids Combined as Esters (327.5)	40.4	35.9

These results are based on the ether extract being equal to 100 per cent.

Lot 1 Solvent Processed.
Lot 2 Soap and Alkali Processed.

Composition of the Ether Extract from Analysis

	Lot 1	Lot 2
Free Acids of Equivalent Weight 327.5	25.5%	25.8%
Combined Acids as Soap 327.5	0.1	2.4
Water Soluble Acids 254	1.9	2.0
Esters of Higher Alcohols	72.7	70.1
Total	100.2	100.3

The composition of these ether extracts was calculated from the listed determinations as follows:—

Free Acids calculated to an equivalent weight of 327.5 since this figure was established under determination seven (7); that is, where the total ether soluble acids were obtained after removal of the unsaponifiable matter and their equivalent weight found to be 326. Also 327.5 is the average molecular weight for the fatty acids in wool grease as determined by Lewkowitsch.[4]

Combined Acids as Soap. There is some doubt in our mind as to the exact nature of this combined acid, whether it exists as a soap or as some other material. However, it is possible that it is soap which has been carried down by the other substances which are ether soluble.

Water Soluble Acids of Equivalent Weight 254 appear to be present in small quantities. Their equivalent weight was determined by the method given in a previous report.[3]

Esters of Higher Alcohols are obtained by adding the unsaponifiable matter to the ether soluble acids combined as esters.

Since the unsaponifiable matter (higher alcohols) was obtained only after a thorough saponification, with a corresponding increase in the amount of fatty acids, it suggests that there was no mineral oil present in the wool used.

SUMMARY

One of the laboratory tests used to determine the efficiency of the mill cleaning process for raw or greasy wool, is an extraction test using ethyl ether or carbon tetrachloride. The amount of material extracted indicates the efficiency of the cleaning process. The material obtained is assumed to be residual wool grease, residual oils from those added during processing, and any free fatty acids from any source. Our work has shown that the compo-

sition of this ether extractable material is approximately the same, regardless of the method used to clean the wool. It appears, in our case, to be made up of some free acids plus a large amount of esters, presumably of the higher alcohols, the general composition being similar to that of wool grease.

The ether extractable material obtained for this work appeared to be entirely residual wool grease in both cases, any oil used in processing being entirely removed in backwashing. It appears that oils added during processing are more easily removed in subsequent scouring operations, than residual wool grease retained from the original raw stock scour.

ACKNOWLEDGMENT

This investigation was made possible by a grant from the Textile Foundation to the American Association of Textile Chemists and Colorists. We wish to express our appreciation for the aid given.

Bibliography

[1]A.S.T.M. Standards for September 1937, page 157.
[2]American Dyestuff Reptr. *27*, P9 (1938).
[3]American Dyestuff Reptr. *27*, P10 (1938).
[4]Lewkowitsch, J. Soc. Chem. Ind., *11*, 135 (1892).
15, 14 (1896).

Bibliography on the Chemistry of Wool*

ARTHUR L. SMITH and MILTON HARRIS

INTRODUCTION

THIS bibliography is limited to publications dealing principally with the more fundamental aspects of the chemistry of wool. Publications relating to industrial processes and to physical testing have been included only if they bear upon the interpretation of chemical properties. Although it has been necessary to exercise personal judgment in the selection of papers to be included, no paper has been excluded because of the doubtful validity of the data or theories given in it. The chief sources of material were Chemical Abstracts, British Chemical Abstracts, and Chemisches Zentralblatt, and wherever possible, abstracts were taken directly from these journals.

The bibliography has been compiled as part of a program of research on the chemistry of wool which is being done at the National Bureau of Standards for the American Association of Textile Chemists and Colorists under the Research Associate plan.

ACKNOWLEDGMENTS

We wish to acknowledge the financial aid given this work by the Textile Foundation, Incorporated, the Chemical Foundation, Incorporated, and the Eavenson & Levering Company. We also wish to express our appreciation to Mr. Alban Eavenson, Chairman, and the other members of the Committee on the Chemistry of Wool, American Association of Textile Chemists and Colorists, for their helpful suggestions.

* Publication approved by the Director of the National Bureau of Standards of the U. S. Department of Commerce.

CONTENTS†

Acid, Absorption of
  Determination of
  Effect of
Alkali, Absorption of
  Determination of
  Effect of
Amino Nitrogen
Bacteria, Enzymes and Fungi
Bromination
Carbonizing
Chemical Constitution
  Amino Acids
  Intermediate Hydrolytic Products
  Nitrogen
Sulfur
Chlorination
Cystine
Damage, Determination of
Deamination, Amino Nitrogen
Dielectric Constant
Dyeing, Mordant
  Theory of
Elastic Characteristics
Electrokinetic Properties
Enzymes
Felting
Fibers, Determination of, in Mixtures
Fulling
Fungi
Halogenation
Heat, Effect of
Heat of Combustion
Heat of Hydration
Heat of Neutralization
Isoelectric Point
Light, Effect of
Milling
Miscellaneous Reagents, Effect of
Moisture, Absorption of
  Determination of
  Effect of
Molecular Weight
Mordanting (Dyeing)
Nitrogen
Oxidation
Photochemical Decomposition
Reduction
Specific Gravity
Specific Heat
Structure
Sulfur
Swelling
Tanning
X-Ray

†The contents indicate the complete bibliography, of which only a portion appears in this issue.

ACIDS, Absorption of

1.—Compounds of Wool With Odorless Amines and Acids.

D. Vorländer and A. J. Perold. *Ann. 345,* 288-302 (1906). In the series aniline, chloroaniline, and dichloroaniline hydrochlorides the amount of the absorption is in the same order as the dissociation of the salt. The absorption of different acids is not in the order of their relative strengths, probably because in a heterogeneous system adsorption, diffusion, capillarity, etc., play a part in the additive process. With acids of similar chemical character, however, the amount of absorption is in the order of their conductivities. Neutral salts are not absorbed by wool, but potassium hydroxide, tetramethylammonium hydroxide, and p-benzene-azophenyltrimethylammonium, hydroxide are very rapidly taken up.

2.—The Chemical Function of Textiles.

L. Vignon. *Rev. gén. mat. color. 11,* 15 (1907). A continuation of the author's work on the acid and basic nature of various fibers. Silk, cotton, and wool of known weight were suspended in 1.0 and 0.1% solutions of sulfuric acid and barium hydroxide. The solutions were analyzed and the ratio of acid or base absorbed by 100 g material to that remaining in 100 g of solution was determined.

3.—Studies on Adsorption in Solution. I. Taking Up of Acids by Wool.

G. Georgievics and A. Pollak. *Monatsh. 32,* 655-75 (1911). The air-dried wool was treated with dilute acids to constant weight. Sulfuric, hydrochloric, oxalic, succinic and acetic acids were used. The taking up of acids by wool is a case of adsorption which runs between certain limits. Temperature variations have only slight influence on these results.

4.—The Absorption of Acids by Wool.

M. Fort and L. L. Loyd. *J. Soc. Dyers Colourists 30,* 5-12 (1914). Wool material was treated with 100 ml of an aqueous solution of varying percentages (1 to 12) of sulfuric, hydrochloric, oxalic, acetic, and formic acids. After 1 hour the aqueous solution was poured off and the free acid removed by washing 3 times with boiling water. Wash water and extract were combined and titrated. The percentages of acids permanently retained when worked out on a molecular weight basis give figures which are similar to the molecular weights of the acids and indicate that these acids are permanently retained as additive salts of wool substance or its hydrolysis products. Comparison of amount of acid remaining after extracting with boiling water with amount retained after washing in cold water, leads to provisional formulas Wool. $2H_2SO_4$, Wool. 2HCl, Wool. 2H.COOH, etc., indicating formation of an additive salt.

5.—Adsorption of Acids by Wool.

W. P. Dreaper. *J. Soc. Dyers Colourists 30,* 52-3 (1914). In a recent paper by Fort and Lloyd (preceding abstract), the acid absorbed by wool was estimated by direct titration, and in their paper they state that the wool gave up a substance which had an alkaline reaction with methyl orange. Dreaper recently pointed out that this method of estimating acid absorbed by fiber is open to criticism, and apparently Fort and Lloyd have not taken this disturbing factor into account.

6.—Absorption of Acids by Wool.

M. Fort and L. L. Lloyd. *J. Soc. Dyers Colourists 30,* 53 (1914). Reply to the preceding abstract.

7.—The Adsorption of Some Acids and Nonelectrolytes by Wool.

Kolloid-Z. 14, 319-21 (1914). Phosphoric and salicylic acids, in spite of their being strongly adsorbed, are characterized by very small x values, a confirmation of the view of Georgievics that the x value varies with the strength of the acid. Acetone and saccharose show extremely small adsorption exponents lying in the neighborhood of 1. The adsorption is thus in greater part due to a formation of solid solution.

8.—The Absorption of Sulfuric Acid by Wool With Some Notes on the Theory of Dyeing.

W. Harrison. *J. Soc. Dyers Colourists 34,* 57-8 (1918). The author and others observed (*Trans. Faraday Soc.*, Apr., 1910) that the positive electric charge acquired by wool after boiling with dilute sulfuric acid solution changed to negative when boiling water was passed through the wool, which showed that the acid had been removed. The acid function of wool (corresponding to a negative charge) appears therefore to be predominant. Harrison found that after 24 extractions practically all the acid was removed, and the wool had no more affinity for acid colors than untreated wool. The author concludes that the dyeing of wool with acid dyestuff is a colloid-chemical problem and not an ordinary chemical reaction.

9.—Colloid Chemistry and the Absorption of Acids by Wool.

M. Fort. *J. Soc. Dyers Colourists 35,* 280-1 (1919). Fort wishes to correct certain statements by Harrison (cf. preceding abstract) relating to the absorption of acids by wool.

10.—Action of Acids on Wool.

W. Harrison. *J. Soc. Dyers Colourists 36,* 17-8 (1920). Reply to M. Fort's criticism of Harrison's work.

11.—Absorption of Acids by Wool. I. Summary of the Literature.

H. Wilkinson and A. G. Tyler. *J. Soc. Dyers Colourists 44,* 241-5 (1928). A review with 42 references to the literature.

12.—Absorption of Acids by Wool. II. III. An Examination of the Experimental Data.

H. Wilkinson and A. G. Tyler. *J. Soc. Dyers Colourists 44,* 369-76 (1928). In agreement with several other workers it was found that the equilibrium between the acid absorbed by the wool and the acid remaining in the liquor was represented by the equation $y = a \log bx$, in which $y =$ the percentage of acid absorbed by the fiber (Cf), $x =$ the percentage concentration of the acid left in the bath (Cs), and a and b are constants. These findings and those of other workers are shown in charts or curves. In this study the observations were made on the absorption (or combination) in the wool phase when immersed in the liquid phase, in which the concentration of the acid in the liquid phase was gradually diminishing until equilibrium was reached. In part II the attempt was made to obtain conditions in which the wool phase would be relatively large and the liquid phase small. The results indicate that under these conditions of equilibrium between absorbed acid and acid concentration the same equation holds. The absorption of acids by wool is a chemical reaction similar to those discussed by Loeb (cf. "Proteins and the Theory of Colloidal Behavior," p. 42 *et seq.*

13.—The Adsorption of Certain Acids by Wool.

W. W. Padden. *J. Phys. Chem. 33,* 1107-8 (1929). At the temperature of boiling water wool adsorbs tartaric acid much less than it does either hydrochloric or sulfuric acid. The adsorption curves show no evidence of the formation of chemical compounds.

14.—The Absorption of Acid by Wool.

H. J. Henning. *Angew. Chem. 47,* 771-2 (1934). The acid absorption was determined with hydrochloric acid solutions of different pH values. A plot is presented of initial against final equilibrium pH values where the points fall on the curve which intersects the 45° line at the isoelec-

tric point of 5.8. This is about 1 unit higher than the value determined by Elöd (4.9) but agrees well with Speakman's value of 6.1.

15.—Titration Curve of Wool Keratin.
J. B. Speakman and E. Stott. *Trans. Faraday Soc. 30,* 539-48 (1934). From measurements of the swelling of wool fibers at various acidities, the isoelectric point was found at a pH of 4.8. Sulfuric acid behaves mainly as a monobasic acid in reaction with wool. Wool does not combine with alkali below pH 7. From the titration curve, the composition of wool was inferred. The fibers consist of long parallel peptide chains bridged across by salt linkages, without an excess of acid side-chains.

16.—The Acid-Combining Capacity of Wool.
J. B. Speakman and E. Scott. *Trans. Faraday Soc. 31,* 1425-32 (1935). The titration curves of wool with hydrochloric, sulfuric, chloracetic, oxalic, and orthophosphoric acids were determined with the glass electrode and show that oxalic and phosphoric acids are monobasic in reaction with wool. At high pH, sulfuric acid is more nearly monobasic than dibasic. At low pH, chloracetic acid combines to a far greater extent than hydrochloric acid at the same pH and exhibits a greater heat of reaction and greater swelling of the wool fiber. The hypothesis is advanced that concentrated solutions of weak acids, because of the higher swelling pressure developed, can separate the sheets of covalently linked peptide chains and liberate amino groups for combination with acid. At the surface of the fiber some amino groups are always available; hence cataphoretic determinations of the isoelectric point of wool are not valid for the fiber as a whole.

17.—Titration Curves of Protein Fibers.
Dorothy J. Lloyd and P. B. Bidder. *Trans. Faraday Soc. 31,* 864-8 (1935). The combining powers of purified collagen fibers from ox hide, silk fibroin fibers, purified horsehair and isoelectric gelatin were determined for the pH range of 1 to 13. A rather wide isoelectric "zone" was found. The more compact the fiber, the wider was the "zone." Between the pH range of 3 to 9 both the amino acid constitution and the structure of the fiber played an important role in the combination, while at pH values of less than 3 or greater than 11.5 the sudden increase in the amount of acid or alkali combined (accompanied by disruption of the fiber) is nearly independent of the amino acid constitution of the protein.

See 191, 197, 205, 208, 319.

ACIDS, Determination of.

18.—Detection and Determination of Free Sulfuric Acid in Wool Fabrics.
E. Philippe. *Mitt. Lebensm. Hyg. 8,* 104-8 (1917). The extraction of weighed portions of the fabric with hot water and the titration of the united and concentrated acid solutions gives unsatisfactory results. The method recommended is as follows: Portions of the cloth are cut into small pieces and placed in an Erlenmeyer flask. An excess of ammonium hydroxide is added and allowed to act for some time with occasional shaking. The solution is then filtered through a small filter, and the flask and contents washed with water until no alkaline reaction is shown. The sulfate is determined in the united filtrates by the usual barium sulfate method.

19.—Volumetric Determination of Sulfuric Acid Included in Wool.
O. Macchia. *L'Industria chimica 4,* 663-5 (1929). From 3 to 5 g. of wool is placed in a beaker with a small quantity of water, and sodium carbonate solution added until the reaction is alkaline to phenolphthalein, and the extract is then filtered through a Gooch filter (no padding). The wool fibers are washed with boiling water, and the filtrate is acidified with hydrochloric acid, after which the sulfate is determined by the benzidine method. Amounts of sulfate of 1 to 2 per cent total are determined by this method within 1 per cent.

20.—Chemical Affinities of Wool.
M. J. Rouffin. *Rev. gén. mat. color. 36,* 140-3 (1932). A curve relating mg. of sulfuric acid per liter of bath to the percentage of sulfuric acid in wool starts at 0.4 per cent as the quantity to neutralize the natural alkalinity of the wool, rises sharply to 2.5 per cent, and then the slope decreases, approaching horizontal. A table is given for estimating the acidity of a wool sample by boiling 10.0 g. of wool in 500 ml. of distilled water and titrating a 250 ml. sample. There is a brief discussion of the effect of this acid distribution on dyeing operations.

21.—Determination of Acids in Wool with Particular Reference to Dyed Goods.
S. R. Trotman and G. N. Gee. *J. Soc. Dyers Colourists 48,* 321-5 (1932). Tris presents a comparison of the ammonia triethanolamine, sodium bicarbonate, magnesium carbonate, Woodmansey, terephthalate and sodium acetate methods.

22.—Some Factors Which Affect the Determination of Acidity in Wool.
S. R. Trotman and G. N. Gee. *J. Soc. Dyers Colourists 49,* 132-4 (1933). The sodium acetate and magnesium carbonate methods of determining the acidity of wool were found only slightly affected by sodium sulfate and dyestuffs. Oleic and stearic acids are recorded by the sodium acetate steam method. The acidity of wool dyed with formic or acetic acid was found to be about as great as when sulfuric acid was used.

23.—The Determination of Sulfuric Acid in Wool.
J. Barrett. *J. Textile Inst. 26,* T87-92 (1935). Sulfuric acid is extracted from wool with a 0.5 per cent solution of pyridine in one-half hour and titrated directly with sodium hydroxide. The method is compared with the terephthalic acid and triethanolamine methods.

See 43.

ACIDS, Effect of.

24.—Theromochemistry of Wool and Cotton.
L. Vignon. *Compt. rend. 110,* 909-910 (1890). The heat developed by the action of normal solutions upon 100 g. of unbleached wool at 11 to 12° is as follows:—

	KOH	*NaOH*	*HCl*	H_2SO_4
Spun wool.....	1.16	1.15	0.95	0.99 Cal.
Combed wool..	1.37	1.10	1.00	1.05 Cal.

The rise of temperature ceases after about five minutes.

25.—Action of Nitrous Acid on Wool.
Alexander P. Lidoff. *J. Russ. Phys. Chem. Soc. 32,* 766-774 (1900). The action which hot nitric acid exerts on wool with the production of a yellow color is found to be due to the nitrous acid formed when the nitric acid is heated. The intensity of the color increases with the proportion of nitrous acid present. The color which nitric acid imparts to wool is, however, perfectly stable towards sunlight, while that given by nitrous acid undergoes rapid change, unless the wool be subsequently dipped into cold nitric acid, when the color becomes stable to light. Experiments made on the change of weight occurring when wool is nitrated showed in the majority of cases a loss of weight varying between 2.19 and 21.9 per cent, although in one case an increase of 1.98 per cent was observed. The nitrated wool feels coarser to the touch than before treatment and reacts readily in the cold with ordinary reducing reagents, the yellow color being converted into a dark brown. The nitrated wool, after perfect washing, is acid towards litmus and at a temperature of 50 to 60° decomposes carbonates with the evolution of carbon dioxide, the color of the wool being changed to brown. It darkens when heated in a vacuum at 110 to 120° and afterwards

chars; it is comparatively readily acted on by dyes. Nitrated wool decomposes potassium iodide solution with precipitation of iodine both in the fiber and in the solution. The coefficieint of acidity (the number of milligrams of potassium hydroxide fixed by 1 gram of the substance when acted on by N_2 alcoholic potassium hydroxide for 12 hours) of the unaltered wool has a mean value of 88, while that of the nitrated product is 169. If the nitrated wool after absorption of potassium hydroxide be washed with alcohol until it has a neutral reaction, it will be found to be strongly alkaline on placing in water, owing to the hydrolysis of the unstable alkali compound. Nitrated wool is not hygroscopic, and it contains less nitrogen than the raw material. The iodine values for wool before and after nitration have the mean values 18.4 and 4.7 respectively. The action of nitrous acid on wool may be regarded partly as a saturation of the free bonds of the molecule with nitro- or nitroso-groups, and partly as an action of nitrous acid on the amino-groups present, to which is due the increase produced in the acid functions.

26.—The Action of Sulfuric Acid on Wool Fiber.

James Stott. *Leather World 4,* 678-80 (1911). A cold dilute solution of sulfuric acid causes the wool fiber to give off minute bubbles of air and gas, and leaves the scales flattened. When the fibers are soaked and heated in a dilute solution of sulfuric acid the scales rapidly dissolve, and leave a core of longitudinal striations which later dissolve into a brown liquor. If the heating is done in concentrated sulfuric acid the fibers disappear much more quickly. Bubbles are given off, the fiber becomes like jelly and soon dissolves. Cold concentrated sulfuric acid causes the scales to break away and float in the surrounding fluid. Sulfuric acid then, of any strength, would tend to dislodge the scales so that the friction of ordinary wear would reduce the fiber to the core. Photomicrographs illustrate clearly the changes in the fiber.

27.—The Effect of Certain Agencies Upon the Color and Dyeing Properties of Wool and Silk.

M. Fort. *J. Soc. Dyers Colourists 32,* 184-7 (1916). The browning of wool upon exposure is largely ascribed to degradation of free amino compounds. These treatments all tend to develop free amino groups in the wool. The brown color may be largely removed by treatment with acid and stoving, and a preliminary treatment with sulfuric acid prevents the discoloration of the above treatments to a great extent. Stoving appears to embrace two functions: first, that of an acid; second, that of a reducing agent. Strong acids develop a coloration which disappears to a considerable degree upon dilution. While heat caused some browning in a reducing atmosphere the browning is much greater in an oxidizing atmosphere.

28.—Effect of Sulfuric Acid on the Durability of Wool.

M. Fort. *J. Soc. Dyers Colourists 35,* 280 (1919). Discussion.

29.—Coloring of Wool and Silk With Strong Acids.

P. Waentig. *Textile-Forsch. 1,* 59-63 (1919). If boiling 50 per cent sulfuric acid or fuming hydrochloric acid is poured onto wool in the presence of a few crystals of sugar, a red color develops in a short time. Without the sugar, pure wool gives very little color, at most only a faint rose tint, but in the presence of considerable quantities of cotton, artificial silk, or other cellulosic substances or of substances such as pentosan, which yield furfural, a decided red color is produced. The presence of fat in the wool leads to a brown color.

30.—Harmful Action of Strong Acids on Wool.

M. Becke. *Textilber. Wiss. Ind. Handel 2,* 194-5, 213-5, 230-1 (1921).

31.—Action of Acids on Wool.

S. R. Trotman, E. R. Trotman and J. Brown. *J. Soc. Chem. Ind. 47,* T45-9 (1928). By immersing degreased wool fabric in hydrochloric, sulfuric or acetic acids from 0.01 to 1.0 *N*, the amount of acid removed was determined in some cases by titration of aliquots during the reaction. Hydrogen sulfide is formed, sulfuric acid producing more than hydrochloric acid. The acid shows nitrogen equivalent to 0.02 per cent of the sample. The amount of sulfuric acid taken up apparently passes through a maximum below 0.1 *N* and decreases; hydrochloric acid increases with concentration up to *N*. Sulfuric acid 70 per cent, has very little effect on wool, probably because the viscosity of the surface film is so great that diffusion of dissolved protein is very slow. Wool treated with strong sulfuric acid must be washed very rapidly for removal of the acid. Consistently lower results were obtained when the wool was agitated with 61 and 70 per cent H_2SO_4 or with dilute hydrochloric acid, than without agitation, which indicates that the presence of a protective film is an important factor. Hydrochloric acid protects the carbonyl groups from condensing with semi carbazide; sulfuric acid does not. The tensile strength varies inversely with the amount of absorbed acid.

32.—The Action of Nitrous Acid on Wool and Reactions of the Product Formed With Azo Components.

H. I. Waterman and J. Groot. *Chem. Weekblad. 25,* 18-22 (1928). "Diazotizing" wool after nitrous acid treatment and boiling causes practically no decrease in the amount of nitrogen. This may be adduced as an argument against the assumption of the formation of a real diazo compound in the fiber. Considerably more H-acid is removed from the bath by wool after treatment with nitrous acid than corresponds to the quantity of nitrogen liberated during the treatment; this probably is due to adsorption by the fiber. A yield of about 0.20 per cent nitrogen was obtained on boiling; it can be raised by prolonging the action or by increasing the nitrous acid concentration. Whether nitrous acid, which might have been absorbed by the fiber, or tyrosine is an essential component in dye formation is not settled.

33.—Physico-Chemical Studies on the Structure of Wool Hair After Treatment With Alkali, Acids, and Chlorine.

Ernst Tanzer. *Wiss. Arch. Landw. Abt. B, Arch Tierenahr. u. Tierzucht 4,* 297-346 (1930). Wool from several breeds of sheep was treated with hydrochloric, sulfuric, nitric, and acetic acids, chlorine water, and chloral hydrate. The wool was then investigated as to histological changes, change in weight, fineness, flattening, hygroscopic properties, tensile strength, elasticity, polarization, reaction with methylene blue, biuret test, reaction with Millon's reagent, and Allworden's reaction.

34.—Action of Nitrous Acid on Animal Fibers, and Reactions of the Products Formed With Azo Components.

M. J. Van Tussenbroek. *Chem. Weekblad 28,* 62-5 (1931). The question is reviewed as to whether nitrous acid forms reactive diazonium compounds with amino acids of the fiber.

35.—The Strength of Dyed Wool.

G. Skipton. *Dyer 67,* 308-9, 362-3 (1932). A general discussion of the effect of acids and alkalies on wool and their use in dyeing.

36.—Damages to Wool Caused by Acids.

W. Zu. *Z. ges. Textile-Ind. (Klepzig's) 36,* 48-9 (1933). Experiments carried out to test the action of water and of various concentrations of sulfuric, acetic, and formic acids at boiling temperature for several hours showed that the addition of

as much as 12 per cent sulfuric acid still exerts a protective action, 6 per cent sulfuric acid maintains its protective action for nearly 5 hours, 3 per cent sulfuric acid contributes little to any fiber damage, and intensive washing hardly removes half of the absorbed sulfuric acid. The rinsing may be omitted with baths containing less Glauber salt. It is claimed that sulfuric acid increases the light sensitivity of wool. Such a tendency is decreased by the presence of the dye, which must be destroyed first before the fiber can be attacked.

37.—Action of Sulfuric Acid on Wool and the Conditions of Scouring.
O. S. Khovanskaya. *Trans. Butlerov. Inst. Chem. Tech. Kazan No. 2,* 67-72 (1934). Various specimens of partly and completely scoured and refined wool were treated with standard sulfuric acid solutions under different conditions. The consumption of acid was determined by titrating with potassium hydroxide. The results show that the chemical consumption of sulfuric acid depends entirely on the wool fat content and its potassium and the mineral impurities. The adsorption of sulfuric acid varies chiefly with the grade of wool and is little influenced by the degree of fiber contamination. The two processes are completed in 2 hours in the cold and in 30 minutes at 30° C.

38.—Reaction of Wool With Strong Solutions of Sulfuric Acid.
Milton Harris, Ralph T. Mease, Henry Rutherford. *Research NBS 18,* 343-350 (1937). Data on the effect on wool of treatment with solutions of sulfuric acid of different concentrations at 5, 25, and 50° C. for 15 minutes and of an 80 per cent solution of sulfuric acid at 25° C. for different lengths of time are presented. The results suggest that strong sulfuric acid reacts with the basic groups in wool to form sulfamic acid derivatives. The acid-combining capacity increases in proportion to the number of sulfamic acid groups formed.

39.—Acid Degradation of Wool Keratin.
Mildred Barr and Rachel Edgar. *Iowa State Coll. J. Sci. 10,* 129-34 (1936). Wool was treated for 10 minutes with concentrations of 0.25 to 8.87 *N* hydrochloric acid at 25° and with concentrations of 0.25 to 0.75 *N* hydrochloric acid and 0.06 to 0.70 *N* sodium chloride for 1 hour at 100° C. The changes in the keratin were followed by determinations in weight, nitrogen and sulfur content, and wet breaking strength. At 25°, weight and sulfur and nitrogen contents were not much affected, but wet breaking strength decreased to about 50 per cent in 7 *N* hydrochloric acid. At 100°, weight decreased little, sulfur and nitrogen decreased 15 to 20 per cent for 0.75 *N* hydrochloric acid and wet breaking strength 85 per cent for 0.50 *N* hydrochloric acid. Salt had little effect.

40.—The Acid and Alkaline Degradation of Chlorinated Wool.
Florence Barr, Mildred Barr and Rachel Edgar. *Iowa State Coll. J. Sci. 10,* 145-50 (1936). The degradation of wool treated with 0.06 *N* hypochlorous acid for 1 hour at 25°, 0.5 to 6.0 *N* hydrochloric acid for 10 hours at 25°, 0.25 to 0.75 *N* hydrochloric acid for 1 hour at 100°, or with 0.05 to 0.2 *N* sodium hydroxide for 10 hours at 40° has been followed by determinations of weight, nitrogen or sulfur content, and wet breaking strength of the residual yarn. The degradation of chlorinated wool by acid in 10 hours at 25° exceeded that of wool as measured by sulfur content or wet breaking strength; at 100° the percentage loss in sulfur was greater than that in weight, nitrogen or wet strength. Sodium hydroxide in 10 hours at 40° dissolved the same amount of sulfur from chlorinated wool as from wool, but decreased the nitrogen content and weight of the chlorinated wool more. The wet strength of chlorinated wool was completely destroyed in 1 hour at 40° by 0.05 *N* sodium hydroxide. The residual chlorinated wool decreases in nitrogen and sulfur content with increasing concentration of acid or alkali.

See 47, 78, 79, 80, 81, 82, 98, 101, 133, 157, 183, 250, 323.

ALKALIES, Absorption of.

41.—Selective Absorption from Soap Solutions.
Harvey A. Neville and Milton Harris. *Research NBS 14,* 765-770 (1935). RP801. Wool in soap solutions adsorbs alkali and soap at the interface and the aqueous medium becomes more acid.

See 2, 15, 17.

ALKALIES, Determination of.

42.—New Method for the Estimation of Alkali With Special Application to Wool.
H. R. Hirst and A. T. King. *J. Textile Inst. 17,* T94-100 (1926). Existing analytical methods, when applied to the determination of alkali in wool, do not give correct results. Wool placed in water containing terephthalic acid in suspension yields all of its alkali to the acid as sodium terephthalate in solution. The sodium terephthalate thus formed may be estimated gravimetrically by filtering out the unchanged terephthalic acid, adding dilute sulfuric acid to the filtrate to convert the sodium terephthalate to terephthalic acid, and filtering and weighing this. This method is used with dyed fabrics which bleed and thus would obscure the indicator changes of the more accurate volumetric method. In the latter method, with bromophenol blue as indicator, a liquid containing terephthalic acid and sodium terephthalate remains purple until the whole of the salt is converted into acid, when a further addition of sulfuric acid changes the indicator. By this method a measured quantity of alkali, whether sodium hydroxide, sodium carbonate, or soap added to wool can be quantitatively recovered. By using this method in conjunction with that for estimating soap (*C. A. 16,* 3212) the amounts of alkali present as soap and sorbed alkali, respectively, can be determined. Estimation of sulfuric acid in wool. Ibid., T101-3. A measured solution of standard sodium terephthalate is added to the wetted sample of wool and the subsequent procedure is the same as that described for the estimation of alkali.

43.—The Use of Methyl Green for Detecting Traces of Alkali in Fibrous Materials.
Ellis Clayton. *J. Soc. Dyers Colourists 51,* 387-8 (1935). A dilute solution of methyl green (0.1 per cent), especially when used at a temperature of 80-100°, is a good reagent for the detection of minute traces of alkali in textile fibers. A standard 0.1 per cent solution in distilled water was prepared. One ml. of this solution in 200 ml. of distilled water was practically unaffected when boiled in a platinum dish for 30 seconds, with similar results when repeated in the presence of 0.25 g. purified wool. One ml. of a 0.1 per cent solution of methyl green, 200 ml. of distilled water and 0.25 ml. of 0.01 *N* sodium hydroxide become decolorized almost completely on boiling.

44.—Hydrolytic Cleavage of the Disulfide Group, A Contribution to the Chemistry of Keratin.
Alfons Schoberl. *Collegium,* 412-21 (1936). Disulfides easily hydrolyze, especially in alkaline solutions, to sulfhydryl (RSH) compounds and sulfenic acids (RSOH). The latter split into ketonic acids and hydrogen sulfide (H_2S). Wool is readily attacked by alkali or boiling water; after boiling wool 14 days the solution contained 46 per cent of soluble matter, 36.2 per cent of hydrogen sulfide and 34.8 per cent of ammonia. Wool boiled with *p*-hydrazinebenzoic acid gives a yellow color which may be a hydrazone from a ketonic acid. Wool is reduced by thioglycolic acid without the formation of hydrogen sulfide;

alkali is necessary for this reduction, probably because hydrolysis precedes reduction.

ALKALIES, Effect of.

45.—The Action of Caustic Soda on Wool.

J. Merritt Matthews. *J. Soc. Chem. Ind.,* 685 (1902). Matthews finds that whereas with weaker solutions, the wool is turned yellow and even disintegrated, when caustic soda solution of 80° Tw. is used for from five to ten minutes at a temperature of 18°, the wool is increased in tensile strength, is whitened in appearance and has imparted to it a high luster and a silky feel and scroop. The color is very similar to that of a bleached yarn and what is of importance too, is that the mercerized wool, as it may be termed, has its dyeing qualities notably improved. The increase *in* tensile strength was 36 per cent, and in elasticity nearly 80 per cent. When the untreated and the treated wools were examined under the microscope, it was found that the treatment had caused the scales so characteristic of the ordinary wool fiber to fuse together and become obliterated, so that the fiber appeared much smoother in outline and more transparent. Untreated wool gave 3.42 per cent of sulfur, while after treatment the same wool showed 0.53 per cent.

46.—The Effect of Alkaline Scouring Agents on the Strength of Woolen Yarns.

J. Merritt Matthews. *J. Soc. Chem. Ind.,* June 30, (1905). The effect of different scouring agents is given in detail, in which different temperatures and different concentrations of scouring solutions were used. The agents employed were hot water, soap, soda ash, caustic soda, ammonia, and borax solutions.

47.—Modification of Textile Fibers by Alkalies and Acids and Their Consequences in the Textile Industries.

E. Seel and A. Sander. *Z. angew. Chem. 29,* I, 261-5 (1916).; *J. Soc. Chem. Ind. 35,* 886. Chemical damage of the wool fiber, such as would depreciate its technical value, may be detected by microscopical examination under high magnifications (700-1000). Wool may be boiled with 1 per cent sulfuric acid for an hour or more, under conditions comparable to those of the acid and chrome-mordant dye baths, without sensible damage, and microscopical examination reveals no structural modification of the fiber. The action of alkalies, however, is very injurious; caustic alkalies act more powerfully than the carbonates, but ammonia is only perceptibly harmful on heating in fairly strong solutions. A series of photomicrographs shows the characteristic modification of the wool hair after the action of a 1 per cent solution of sodium hydroxide for 15 minutes at from 40 to 80°. Different varieties of wool differ in their degree of resistance. The initial indications of attack take the form of longitudinal striations due to the wrinkling of the epithelial scales, so that the surface of the hair assumes somewhat the appearance of a withered apple. For this observation the high power of the microscope must be focused sharply on the surface of the hair; otherwise the longitudinal arrangement of the interior layer of cells may lead to false conclusions. Water or glycerol jelly is the best mounting medium. The wrinkling proceeds from a mere swelling of the scales to the formation of pronounced furrows as the attack advances and the temperature is raised. At 70° disintegration of the epidermis layer begins and at 80° the separation of the cuticle from the fiber layer is complete. Wool which has previously been modified by the action of alkali becomes extremely sensitive to attack by hot dilute sulfuric acid. The apparent striations which are observed in this case differ distinctly from the wrinkling produced by the alkali alone. In alkali dye vats, the destructive action of the caustic alkali may be avoided by the use of carbonates, thiosulfate and ammonia.

48.—Alkali and Weathering Studies With Wool.

J. I. Hardy, et al. *Wyoming Sta. Rept.* 164-9 (1917). Sixteen samples of wool drawn from range ewe fleeces were treated with solutions of 10 per cent sodium carbonate, 10 per cent sodium sulfate, and 10 per cent magnesium sulfate for a period of one week. The average breaking strength as compared with the untreated samples showed little effect produced by the solutions, though the sodium carbonate weakened the fiber the most. Another set of the samples of crude and scoured wool treated with solutions of the same strength once every 10 days or two weeks and weathered showed that the untreated crude wool had a greater breaking strength than the clean wool or any of the treated samples. Again the sodium carbonate produced the greatest effect upon the fibers. It is concluded that the differences are not great and that further work is necessary before definite conclusions can be arrived at.

49.—An Albumose from Wool.

Leon Marchlewski and A. Nowotnowna. *Iszy Zjazd Chemikow Polskich 26,* (1923). A small amount of albumose, giving all the ordinary reactions for albumoses, is obtained by the hydrolysis of wool with solutions of calcium or barium hydroxide.

50.—The Change of Keratin by Alkalies.

M. Bergman and F. Stather, *Collegium,* 109-10 (1925). Treatment with sodium sulfide decreased the cystine (calculated from the sulfur content after hydrochloric acid hydrolysis) in sheep wool and horse hair, but the destruction of the wool structure does not depend on complete decomposition of the cystine.

51.—The Action of Ammonia on Wool.

H. E. Farrar and P. E. King. *J. Textile Inst. 17,* T588-90 (1926). The sulfur content of the original cloth (calculated on the dry weight at 100-105°) was 3.92 per cent. Heating in a bath containing 12 per cent of ammonium hydroxide by weight, and in the proportion of one part of wool to five parts of liquor, for 5.5 hours at 70°, reduced the sulfur content to 2.81 per cent. The wool, though becoming yellow, was not appreciably tendered. By increasing the period of heating, or by dividing the time of heating into successive periods with washing of the wool between treatments and the use of fresh ammonium hydroxide the sulfur content was reduced to 2.1 per cent. Variable amounts of ammonium bisulfide were noted in the liquid, and the wool became tender. At lower temperatures less sulfur was removed.

52.—Effects of Alkalies on Wool. II. Effects of Sodium Compounds, Effects of Potassium Compounds and Temperature.

H. C. Chapin. *Proc. Am. Assoc. Textile Chem. Colorists,* 42-6 (1927). *Am. Dyestuff Reptr. 16,* 90-4 (1927). The strength of wool, measured before and after treatment with water, alkali carbonate solutions, and soap solutions at 50°, show that the effect of small changes in treatment are so apparent as to justify the use of weakening effect as a measure of surface harshening effect, provided there is some direct connection between the two. In solutions of equimolar concentration, sodium carbonate and potassium carbonate have equal weakening effect. The effect of sodium soap is small compared with that of the hot water in which it is dissolved, and much smaller than that of 0.1 *N* sodium carbonate or potassium carbonate solution. Any difference in the effects of sodium and potassium soaps is small. A soap which in water alone weakens wool may in solution with alkali carbonate reduce the weakening effect of the carbonate. A rise of 1° in scouring temperature has about the same weakening effect on wool as a rise of 25 per cent in carbonate concentration when the temperature is near 50° and the carbonate concentration is near 0.2 *N*.

53.—The Protection of Woolen Goods from Damage by Alkalies.

S. R. Trotman. *Textile Recorder 46,* 57-8 (1928). Examples of various types of protection are given.

54.—The Action of Caustic Soda on Wool.

J. B. Speakman. *J. Soc. Chem. Ind. 48,* T321-4 (1929). Wool fibers are disintegrated by dilute solutions of sodium hydroxide, the rapidity increasing with increased concentration of sodium hydroxide up to 15 per cent; beyond this point the strength of the yarn increases until 38 per cent of sodium hydroxide in solution is used. Investigation of the action of caustic solutions on individual wool fibers (not yarn) under carefully controlled conditions showed that (a) the elastic properties of single wool fibers are completely unaffected after immersion in 38 per cent sodium hydroxide solution for 5 minutes at 19°; (b) the immunity of the fibers is due to the low partial pressure of water vapor in equilibrium with 38 per cent sodium hydroxide solution and to the formation of the complex hydrate $2NaOH.7H_2O$ with correspondingly low OH-ion concentration; (c) the 30 per cent increase in the strength of wool yarn after immersion in 38 per cent sodium hydroxide solution is due to the surface gelatinization of the fibers, which binds them firmly together in the dried yarn.

55.—The Formation of Acetaldehyde in the Alkali Cleavage of Proteins.

Otto Riessler with Collaboration of Anneliese Hansen, and Raimund Nagel. *Z physiol. Chem. 196,* 201-12 (1931). Acetaldehyde is obtained by distilling proteins with alkali but not with acid, keratin yielding 0.09 per cent.

56.—The Alkaline Decomposition of Wool Keratin.

Mildred Barr and Rachel Edgar. *Proc. Iowa Acad. Sci. 41,* 170 (1934). The alkaline hydrolysis of wool keratin effected in 12 hours at 25°, 40°, and 55° has been followed by determination of the weight, nitrogen, sulfur, and wet breaking strength of the residual wool fabric. The decrease in weight, nitrogen, sulfur, and wet breaking strength and the ratio of the sulfur of the hydrolysate to that of the residual wool have been shown to be greater, the greater the concentration of alkali or the greater the temperature. The weight of the residual wool has been shown to be a linear function of the alkali concentration. The ratio of sulfur to nitrogen decreased with increasing concentration of alkali or increasing temperature.

57.—Effect of Sodium Hydroxide of Various Concentrations on Wool.

R. Jäger. *Monatschr. Textil-Ind., 49,* 17, 39-40 (1934). Studies were made on the effect of the various concentrations of sodium hydroxide on elasticity, relationship between tenacity and lengthening, shortening and swelling properties.

58.—The Alkaline Mercerization of Wool.

Mildred Barr and Rachel Edgar. *Iowa State Coll. J. Sci. 10,* 45-8 (1935). The mercerization of plain-woven unstoved wool of 0.30 per cent ash and no sulfates, by 16, 29, 38 and 44 per cent sodium hydroxide for 5 minutes at 14° has been followed by weight, nitrogen, sulfur, dry-warp and wet-warp breaking strength and elongation at breaking load. The loss in weight, nitrogen and sulfur, has been shown to decrease with an increase in concentration from 16 to 38 per cent sodium hydroxide and to be greater at 44 per cent sodium hydroxide. At 38 per cent sodium hydroxide the wool lost 1.2 per cent in weight, 1.0 per cent in nitrogen and 5.3 per cent in sulfur. The loss of wet and dry breaking strength was less, the greater the concentration of alkali. At 44 per cent sodium hydroxide the dry breaking strength was 95 per cent and the wet breaking strength but 40 per cent of the corresponding value for the original wool.

59.—Effect of Alkalies on Wool.

M. Harris. *J. Research NBS 15,* 63-71 (1935), RP810; *Am. Dyestuff Reptr. 24,* 562-7 (1935). Data on the effect of various alkaline reagents on the physical and chemical properties of wool yarn are presented. When wool is treated with dilute sodium hydroxide solutions, a rapid occurs. On continued treatment, the sulfur ocurs. On continued treatment, the sulfur content of the residual wool approaches a constant value of about 1.8 per cent. The results indicate that the alkaline treatment has changed a portion of the sulfur to a form which tends to resist further splitting from the molecule. Oxidizing and reducing agents attack the disulfide groups and make wool more susceptible to alkaline treatments. The susceptibility of untreated wool to alkaline reagents appears to be closely associated with the lability of its sulfur in alkaline solutions.

60.—Alkalies and Wool.

Frederick R. Harrison. *Textile World 85,* 2247 (1935). Up to a pH of 12 at 120°F. for 15 minutes, the amount or kind of alkali has no harmful effect on wool, so far as that effect can be measured by tensile strength. Above pH 12, damage is shown by decrease in strength and by yellowing.

61.—Alkaline Degradation of Wool Keratin.

Mildred Barr and Rachel Edgar. *Textile Research 6,* 273-7 (1936).

62.—Mechanism of the Sulfur Lability in the Alkali Degradation of Wool Protein.

J. A. Crowder and Milton Harris. *Am. Dyestuff Reptr. 25,* 264-6 (1936); *J. Research NBS 16,* 475-480 (1936), RP885. It is the purpose of this paper to describe the behavior of sulfur in wool under conditions which are very different from those ordinarily used in studies on sulfur lability and to point out a probable mechanism by which sulfur is split from wool during alkali treatment. The data indicate that the primary process in the alkali cleavage of the disulfide linkage consists in a hydrolytic rupture of the disulfide group with the formation of a sulfhydryl compound and a sulfenic acid. The sulfenic acid is extremely reactive and unstable in alkaline solution and immediately loses hydrogen sulfide and forms an aldehyde. The results of the investigation indicate that the existence of labile sulfur in proteins is not an indication that the bulk of the sulfur is present in more than one form.

See 98, 112, 157, 228, 238, 303, 304, 323, 383.

BACTERIA. ENZYMES, and FUNGI.

63.—The Influence of Microorganisms in the Weathering of Wool and Cotton.

S. R. Trotman and R. W. Sutton. *J. Soc. Chem. Ind. 43,* 719D-2 (1934). Pieces of woolen fabrics inoculated with *Bacillus subtilis* at 37.5° showed after 48 hours marked attack on epithelial scales. increased affinity for acid dyes, and decreased shrinking power. After 5 days the fabric becomes quite rotten and disintegrates on boiling with water; the solution containing sulfur gives a precipitate with tannic acid, a strong biuret reaction, but no precipitate with ammonium sulfate. Similar results were obtained with *mesentericus.*

64.—Destruction of Wool by Exposure to the Atmosphere.

S. R. Trotman and R. W. Sutton. *J. Soc. Dyers Colourists, 41,* 121-7 (1925). Wool is readily attacked by microorganisms. Sporeforming bacilli, particularly those which liquefy gelatin. cause the most damage. Cocci are less harmful than bacilli. Different organisms produce damage at different rates, each growing best within certain limits of pH. Damage by bac-

teria causes destruction of the epithelial scales, exposure and liberation of the cortical ctlls and ultimately complete disintegration of the fiber. Fabrics damaged by bacteria have an increased affinity for acid and direct dyestuffs but dye unevenly. They give us more soluble matter than undamaged fabrics when treated for wet processes, and thus undergo a greater loss of weight in chlorinating, bleaching, etc. Damp storage is a common cause of bacterial damage.

65.—Deterioration of Woolen Goods.

J. Merritt Matthews. *Textile World 69,* 195, 227 (1926). The various deteriorating agencies of wool are discussed, with emphasis upon bacterial damage as the most important factor.

66.—Microbiology of Wool.

R. Burgess. *J. Textile Inst. 19,* T315-22 (1928). The essential properties of an efficient antiseptic for the prevention of mildew in woolen goods are described. While many substances such as sodium fluoride, chloramine T, chlorinated phenols, etc., do not inhibit the growth of fungi and bacilli, others such as mercuric chloride, salicylic acid, thallium carbonate, etc., and notably sodium fluosilicate, give better protection. The conditions of testing antiseptic, the effect of the alkalinity or acidity of the cloth under examination. and methods of detecting damaged fibers by staining tests are discussed.

67.—Microbiology of Wool. Enhancement of "Mildew" by Soaps and Vegetable Oils.

R. Burgess. *J. Textile Inst. 20,* T333-72 (1929). Mildew on cellared or aged and stored wool goods is due to mold fungi rather than to bacteria. Soaps, wool creams and the majority of conditioning fluids enhance its development on account of the alkali in them, which. by combining with the wool, renders it more easily attacked. Another factor in the case of hygroscopic soaps is the increase in the range of relative humidity over which mold growth can occur. Vegetable oils such as olive oil enhance mildew growth but to a smaller extent than soap, and in this connection the nutritive value of the oil is important. The presence of foots in the oil does not increase liability to mildew. The commercial conditioning liquid "Hygrolit" and the other fluids resembling it retard the mold growth, as also do the lower fatty acids, such as caproic, caprylic and lauric acids; on the other hand, more complex fatty acids, e.g., oleic acid, favor the growth. Mineral oils have a protective effect and are not used as food by mold fungi. The greenish yellow stains commonly found on mildewed wool are caused by mold action on the soap present. Washing scoured or unscoured wool in several changes of hot water reduces the liability to mildew. The reaction range over which mold growth can occur on wool is considerable, since both acid and alkali conditions favor it. It is recommended that, if possible, the use of conditioning liquids should be discontinued. and water used instead. The practice of dispatching goods in air-tight cases is unsound, since the stagnant conditions so produced favor the growth of fungi by setting up localized regions of moisture condensation.

68.—The Liability of Dyed Wool to Mildew With Special Reference to the Resistance Resulting from Chroming.

R. Burgess. *J. Textile Inst. 21,* T441-52 (1930). Wool dyed by various methods in the laboratory was exposed to conditions favorable for the growth of microörganisms. The results of these tests are tabulated and show that the use of chrome in the dye bath imparts to wool a considerable resistance to the development of the mold fungi chiefly responsible for mildew. Results of tests on the effect of various amounts of chrome indicated that one-half per cent chrome, either as chromium trioxide or chromic oxide imparts a definite resistance to mold growth, while 1 per cent checks it. The results indicate that the resistance imparted by chrome is due to the impoverishment of the wool as a source of the nutriment required by these organisms. Thorough washing off after dyeing or scouring is beneficial and reduces the liability to mildew.

69.—Factors Affecting the Development of Mildew on Wool.

R. Burgess. *J. Soc. Dyers Colourists 47,* 96-9 (1931).

70.—Action of Pancreatin on Different Types of Wool.

Cl. Fromageot and A. Porcherel. *Compt. rend. 193,* 788-9 (1931). The wool of coarser fiber is less resistant to the action of pancreatin. As much as 82 per cent of the initial weight may be lost. The destruction of the fiber takes place in two stages: (1) the rapid solution of the protein holding together the cellular elements, and (2) the slow attack on the cellular elements themselves.

71.—The Enzymic Decomposition of Animal Fibers by Bacteria.

Johann Bartsch. *Melliand Textilber 12,* 760-2 (1931); *Ibid. 13,* 21-4 (1932). This is a discussion of the damages caused by bacteria on wool and silk, the mechanism of their action, and the importance of the investigations for the theory of the fiber structure.

72.—The Cortical Cells of Merino, Romney and Lincoln Wools.

M. T. Gabriel. *J. Textile Inst. 23,* T171-6 (1932). A new retting method was developed for breaking up wool fibers for studying their cellular characters. The method was used in a study of the length of the cortical cells in wools of different origins and breeds.

73.—Pink-Rot of Wool.

R. Waters Massey. *New Zealand J. Agr. 44,* 35-8 (1932). The organism promises to be a very convenient agent to employ in the study of the cellular structure of the wool fiber, inasmuch as it seems to have little or no disintegrating effect upon the cells themselves but rather to dissolve or soften some substance that normally holds the cell very firmly together.

74.—Natural and Acquired Resistance of Animal Hairs to Microbiological Agencies.

R. Burgess. *J. Textile Inst. 25,* T391-400 (1934). The value of the test (*C. A. 28,* 7541[6] involving the use of trypsin solution as a means of determining the resistance of wool and other animal fibers to bacterial attack was further investigated with special reference to raw and processed materials and the action of certain chemical treatments. Considerable variation in resistance to trypsin was shown by unprocessed animal hairs, which may account in part for differences in behavior of these materials during processing and use. Previous results obtained with chrome and Eulan N were confirmed. Chrome, applied as in normal dyeing procedures, gives pronounced protection against bacteria and, to a less degree, to molds which decompose wool. Eulan N gives less resistance than chrome, but, used with it, adds materially to the protective effect. This action is attributed to a chemical modification of the fiber relative to proteolytic enzyme action rather than to a bactericidal effect. Cutch alone imparts inadequate protection, but when combined with ferrous or cupric sulfate or potassium dichromate gives good protection against bacteria. The use of trypsin for indicating fiber damage caused by agents other than microbiological, e. g., damage by mild acid and alkali, is suggested. Recommendations are given for the practical application of the results obtained in cases where wool may be left wet for a time.

75.—Causes and Prevention of Mildew on Wool.

R. Burgess. *J. Soc. Dyers Colourists 50,* 138-42 (1934). The amounts of nutrient substances present influence greatly the susceptibility of wool to mildew in a damp atmosphere. Intense chlorination and treatment with hydrogen peroxide or ultra violet light cause increased susceptibility. For bacterial development actual wetness is probably required.

76.—The Mildew of Wool.

L. Armand. *Tiba 12,* 675-9, 751-5, 831-5, 917-23 (1934); *Ibid. 13,* 23-7 (1935). This is a report on numerous tests, extending over a period of two years, on the inhibiting action of dyes toward the mildewing of wool. Conclusions: The influence of the constitution of the dye is very small, and no dyes were found which. by their presence on the fiber, prevented or notably retarded the development of mildew; the "antiseptic dyestuff" sought by some investigators apparently does not exist. The only definite indication which can be given regarding the effect of the molecule of the dye is that certain electronegative groups (particularly halide, nitro and carboxyl) seem to exert a retarding action on the development of molds; this action occurs with all classes of dyes, but becomes apparent only when there is an accumulation of such groups in the molecule. The preponderating factor in the development of mildew is the presence or absence on the wool of degradation products of the fiber proteins (in confirmation of Burgess' work.) All treatments which remove these products remove the possibility of development of molds; such treatments are equally effective whether carried out before, during or after dyeing. The most important and simplest of these treatments is chroming; the efficiency of chrome dyes is due, not to their constitution, but to the fact that treatment with chrome removes the protein degradation products which are always on the wool. Similar protective action is obtained by subsequent chroming of wool that has been dyed with certain direct dyes. Protection is obtained also by treatment with cupric sulfate, chromium fluoride or formaldehyde of certain direct dyes; but in these cases the action is due to the bactericidal power of the chemicals rather than to removal of the degradation products of the proteins, so that the protective action is much weaker than with chroming. All treatments which increase the degradation of keratin (particularly alkaline treatments such as are used in vat dyeing) favor the development of mildew.

77.—The Use of Trypsin for the Determination of the Resistance of Wool Fibers to Bacterial Disintegration.

R. Burgess. *J. Textile Inst. 25,* T289-94 (1934). Wool fibers can be disintegrated into their component elements, epithelial scales and cortical cells, by exposure to an appropriately buffered solution of trypsin or pepsin. The action of the trypsin solution is similar to that of proteolytic bacteria, but more rapid. It is proposed for adoption as a laboratory method for determining the resistance of wool and other animal fibers to bacterial action. Treatment with chromium or Eulan N, or both, increases the resistance of wool to bacteria.

See 140, 157.

BROMINATION (See halogenation).

See 156.

CARBONIZING.

78.—Carbonization of Wool Containing Vegetable Matter.

W. Harrison. *J. Textile Inst. 9,* 10-13 (1918). The object of this work was to determine the conditions under which wool could be carbonized without loss of strength. The results showed that wool should not be subjected to a temperature above 60° while containing acid in the wet condition. Heating to 100° for 2 hours had little effect on dry wool. Neutralization should be done as soon as possible after carbonizing. The maximum concentration of sulfuric acid which could be used without tendering was 5 per cent. In neutralizing it was immaterial what concentration of soda was used. The amount of acid used in carbonizing was 0.26 g. of sulfuric acid per 5 g. of wool.

79.—Physical Chemistry of the Carbonizing Process.

Alan A. Claflin. *Am. Dyestuff Reptr. 21,* 575-7 (1932). Investigations show that proteins such as wool combine with either acids or alkalies to form salts; this operation is accompanied by swelling. The wool fiber itself acts as a chamber enveloped by a semipermeable membrane. Acids and bases enter the fibers by osmosis and swell them. Salts and concentrated acids depress this swelling. In the carbonizing of wool the fibers swell in the soaking bath, contract during drying, and swell again during the subsequent wetting operations. The changes in physical condition affect the dye-absorbing properties of wool. Residual soaps, oils, hard water, etc., from preliminary operations produce dye-resist spots and blotches on wool.

80.—The Carbonizing Process. A Study of the System Wool-Sulfuric Acid-Water.

M. Harris. *Am. Dyestuff Reptr. 53,* 224-9 (1934). The purpose of this study was to provide quantitative data on the system wool-sulfuric acid-water under conditions similar to those in the soaking, drying, and baking of wool in the carbonizing process, as a basis for the effective study of problems relating to the process. The amounts and rates of absorption of sulfuric acid are reported. Wool treated with acid retains less moisture than untreated wool. When wool is baked, there is a critical moisture content for each concentration of acid in the wool. The physical and chemical breakdown increases with increased concentration of acid and increased temperature of baking. The increase in break-down appears to take place in the first few minutes of baking. The deterioration of wool in the baking process is promoted by the presence of oxygen, moisture, and sulfuric acid. The nature of the system wool-sulfuric acid-water is discussed.

81.—A Study of the Carbonizing Process and Its Effect on the Dyeing Properties of Wool.

B. A. Ryberg. *Am. Dyestuff Reptr. 53,* 230-40 (1934). Experimental work is outlined to show the effect of various factors in the carbonizing of wool by the sulfuric acid method. The dyeing properties of wool are affected by the carbonizing process. Sixteen conculsions show the effect on wool of the various stages of the carbonizing process.

82.—A Fundamental Study of the Wool Carbonization Process, IV. Continuation of Study of Sulfuric Acid Process.

B. A. Ryberg. *Am. Dyestuff Reptr. 24,* 142-9 (1935); cf. *C. A. 28,* 3908[1]. Certain phases of the carbonization process such as treatments for the removal of acid after carbonizing, the effect of various conditions on the vegetable matter, etc., are described. V. Study of aluminum chloride process and its effect upon the dyeing properties of wool. *Ibid. 24,* 150-62 (1935). A comparison of the two methods of carbonizing wool indicates that the sulfuric acid method is more severe in its action on the wool than the aluminum chloride method.

CHEMICAL CONSTITUTION.

See 315.

AMINO ACIDS.

83.—Hydrolysis of Keratin from Horn and Wool.

E. Abderhalden and A. Voitinovici. *Z. physiol. Chem. 52,* 348-67 (1907). Keratins

from horn and wool were hydrolyzed with acid and the resulting solutions analyzed for the various amino acids. The results are compared with previous results for keratin from hair and feathers. Different results are obtained in all cases and indicate that keratin is a mixture of proteins.

84.—*l*-Cystine.

R. A. Gortner and W. F. Hofman. *Org. Syntheses V,* 39-41 (1925). Directions are given for the hydrolysis of human hair and the isolation of *l*-cystine in 5-5.3 per cent yields. The yield from sheep's wool is about 2.6 per cent.

85.—Relation of the Cystine Yield to the Total Sulfur in Wool.

J. Barratt. *J. Soc. Chem. Ind. 46,* T338-41 (1927). The maximum yield of cystine from wool corresponds to 66 per cent of the sulfur present. From hair 70 per cent of the sulfur is recoverable as cystine.

86.—The Chemical Composition of Wool With Especial Reference to the Protein of Wool-Fiber (Keratin).

H. R. Marston. *Australia Council Sci. Ind. Research Bull.* No. 38, 36 pp. (1928). Wools grown under a great variety of conditions in Australia, from various breeds of sheep, and having spinning counts varying from 48 to 74, were investigated. The compositions of all the wool keratins were found to be identical within the limits of experimental errors. Alterations in the experimental technic of the Van Slyke method used in this work for separating the nitrogen of the keratin are described. Because of inherent errors in the method, the quantities of monoamino acids thus estimated must be considered relative rather than absolute values. Therefore, in the following results, the figures for the cystine, tyrosine, and tryptophan contents of wool keratin are considered exact; those for arginine, histidine and lysine, a very close estimate: cystine, 13.1 per cent; tyrosine, 4.8 per cent; tryptophan, 1.8 per cent; arginine, 10.2 per cent; histidine, 6.9 per cent; lysine, 2.8 per cent; "amide" nitrogen, 1.2 per cent; sulfur, 3.58 per cent; and total nitrogen, 17.8 per cent. For determining the acid-combining power of wool keratin by the quinhydrone electrode, the potential difference between the hydrogen electrode and the quinhydrone electrode at normal (760 mm. of mercury) pressure of hydrogen was measured at temperatures varying between 0° and 40°. The isoelectric point, estimated by extrapolation, is pH 3.4 which agrees well with the value of Meunier and Rey.

87.—Sulfur-Containing Amino Acids, VIII. The Quantity of Cysteine in the Fresh Tissue Proteins.

Yuzuru Okuda and Yoshitaro Katal. *J. Agr. Chem. Soc. Japan 5,* 549-60 (1929). Cysteine was determined by means of potassium iodide-potassium iodate with chloroform as indicator in place of starch solution. Hair and wool gave only minute quantities of cysteine.

88.—The Basic Amino Acids of Wool.

H. B. Vickery and R. J. Block. *J. Biol. Chem. 86,* 107-11 (1930). The basic amino acids were isolated from the protein of sheep wool by a modification of the silver precipitation method of Vickery and Leavenworth and were found to be present in the keratin in the following amounts: histidine 0.66, arginine 7.8, and lysine 2.3 per cent. These results agree so closely with those obtained with human hair that it is probable that a marked analogy exists in the chemical composition of the two types of keratin.

89.—The Function of Cystine in Wool Production.

O. H. Keys. *New Zealand J. Agr. 43,* 262-6 (1931). The factors affecting the cystine content of wool are briefly discussed.

90.—Preparation of Cystine.

J. G. Louw. Union S. Africa Dept. Agr., *Rept. Director Vet. Services, Onderstepoort 17,* Pt. 2, 473-4 (1931). Tyrosine-free cystine was prepared from wool by a modification of Folin's method; the yield was approximately 120 g. per 2.5 kg. of scoured wool.

91.—Basic Amino Acids of Wool.

A. Malcolm Stewart and C. Rimington. *Biochem. J. 25,* 2189-92 (1931). A fleece of Australian wool gave histidine 0.55, arginine 6, and lysine 2.2 per cent.

92.—Cystine and Wool Production.

A. H. H. Fraser and J. A. Fraser Roberts. *Nature 130,* 473 (1932). This is a brief review which includes experimental results obtained by the authors in support of an assumption that cystine may be synthesized by the sheep. The hypothesis is advanced that cystine synthesis is a function of the wool follicle.

93.—The Constitution of the Keratin Molecule.

C. Rimington. *Nature 129,* 580-81 (1932). Rimington criticizes the assumption of Speakman and Hirst that every molecule of glutamic acid (I) or aspartic acid (II) has one carboxyl group free to enter into salt formation with an amino group. Wool yields 1.2 per cent of amino nitrogen. Speakman and Hirst must deduct 12.6 per cent by weight of (I) from 12.9 per cent contained in wool since this combines with the 1.2 per cent of amino nitrogen, leaving 0.3 per cent of (I) and 2.3 per cent of (II) free to enter into the type of union they postulate. The question is also raised whether hydroxylysine may not be a constituent of wool. Speakman and Hirst found 0.94 to 1.11 per cent amino nitrogen in the wool they examined; the *e*-amino group of the 2.8 per cent of lysine accounts for only 0.27 per cent. They included 0.82 per cent as being from 10.2 per cent arginine, making 1.09 per cent in all. However, Rimington points out that the guanidine group of arginine does not yield the calculated quantity of nitrogen with nitrous acid.

94.—Methionine in Wool.

J. Barratt. *Nature 131,* 689-90 (1933). A few wools contain 0.5 per cent of methionine based on the dry weight of the keratin. Mueller has isolated about 0.2 per cent of methionine from wool. This compound on hydrolysis with sulfuric acid gives homocystine, which is reactive to the Folin-Marenzi reagent. Only about 3 per cent of the total sulfur is present as methionine, the remaining part being present largely as cystine.

95.—Distribution and Origin of Sulfur in Wool. I. Methionine in Wool.

J. Barratt. *Biochem. J. 28,* 1-5 (1934). The amount of methionine present does not substantially affect previous work on the relation between total and cystine sulfur in wool.

96.—The Isolation of Cystine from Wool Hydrolysates.

G. Toennies and M. A. Bennett. *J. Biol. Chem. 112,* 39-50 (1935). A suitable hydrolyzing agent for the preparation of cystine from wool is 50 per cent sulfuric The humin fraction can be removed from the hydrolysate by salting out with sodium sulfate, and the cystine is rapidly precipitated by cupric ion without oxidative or reductive changes. The best yield obtained was equivalent to 44 per cent of the total sulfur content of the wool. Because of racemization the stage at which the amount of *l*-cystine available for isolation is at its maximum does not coincide with the completion of hydrolysis, and a negative biuret test or a cyanide-nitroprusside test corresponding to the total sulfur content is no proof of completeness of hydrolysis as far as liberation of cystine is concerned. No relation was found between the optical rotation of the hydrolysate and the stage of cystine under different conditions.

See 119, 127, 128, 156, 221, 355, 356, 379.

Intermediate Hydrolytic Products.

97.—Quantitative Method of Distinguishing Between Wool Gelatine and Animal Size, and Some Properties of Wool Gelatine.

A. Herz and C. E. Barraclough. *J. Soc. Dyers Colourists 25,* 274-6 (1909). All animal fibers, wool, goat hair, camel hair, and human hair, yield on boiling a water-soluble substance. This so-called wool gelatin behaves in exactly the same way as glue in the tannin or biuret test. The best way to distinguish analytically between this wool gelatin and glue is to apply in the first test basic lead acetate, and in the second test tannin-salt solution. Wool gelatin precipitates the basic colors, the acid being liberated. Wool gelatin appears to consist of three substances: (a) one that is not precipitated by night blue but which is precipitated by tannin-salt; (b) one that is precipitated by night blue, goes into solution when this precipitate is decomposed by barium hydroxide, and is again capable of precipitation either by night blue or tannin-salt after removal of excess barium hydroxide; (c) one that is precipitated by night blue but remains insoluble and mixed with the insoluble night blue base on decomposing the precipitate by barium hydroxide.

98.—Nature of the Proteins of Wool.

S. R. Trotman, E. R. Trotman and R. W. Sutton. *J. Soc. Chem. Ind. 45,* T20-4 (1926). Woolen fabric was extracted in a large, soxhlet apparatus successively with light petroleum ether, carbon tetrachloride, carbon disulfide, and alcohol when no loss of sulfur occurred. The experiments of Allwörden (cf. *C. A. 10,* 1436) were repeated but his results were not confirmed. Cold N or 0.2 N sodium hydroxide removed 50 per cent of the sulfur in 12 hours; 0.01 N sodium hydroxide removed no sulfur. When cold dilute sodium hydroxide acts on wool the cortex appears to be attacked more readily than the epithelium. This suggests the presence of two proteins. Two proteins were separated from wool by treatment with concentrated hydrochloric acid at 70°, filtering, reprecipitating and purifying. The first protein (A) gave ash 0.40 per cent, sulfur 3.62 per cent, nitrogen 12.50 per cent. The filtrate after removing (A) contained another protein (B) which gave ash 0.10 per cent, sulfur 1.49 per cent, nitrogen 12.68 percent. A considerable proportion of the sulfur is present in firm combination but it may be removed without destroying the protein-like structure. (A) and (B) gave humin nitrogen 2.55 per cent and 2.45 per cent, amide nitrogen 1.20 per cent and 3.90 per cent, diamino nitrogen 12.00 per cent and 34.30 per cent, monoamino nitrogen 86.25 per cent and 59.35 per cent, respectively.

99.—Proteins of Wool. II.

M. Saito. *J. Agr. Chem. Soc. Japan 6,* 1109-24 (1930). The wool was treated with 1 per cent hydrocloric acid under 5 atm. pressure for 5 hours. Ninety per cent of the solid matter was dissolved. By fractional precipitation six albumoses and a peptone were obtained. These are compared.

See 49, 187, 355.

Nitrogen.

100.—Melanin. V. Comparison of Certain Nitrogen Ratios in Black and in White from the Same Animal.

R. A. Gortner. *J. Am. Chem. Soc. 35,* 1262-8 (1913). Analyses, including nitrogen partition, of black and of white wool taken from the same animal show close agreement except that humin nitrogen in black wool is 3.45 per cent in excess, and the amino nitrogen in the filtrate from the bases 2.5 per cent less than that in white wool; but no necessary relationship exists between these fractions. The excess of humin nitrogen is due to the presence of pigment. The total nitrogen of white wool is 16.27 per cent and of black wool 15.11 per cent; the lower nitrogen content of the latter is attributed to the presence of melanin, which contains less nitrogen than the keratin structure. Humin nitrogen is but a part of the melanin nitrogen of the wool. Hydrolysis with a strong acid apparently breaks down the melanin molecule.

101.—Development of Amido Groups in Wool.

M. Fort and L. L. Lloyd. *J. Soc. Dyers Colourists 30,* 73-8 (1914). In attempting to define more accurately the role of amido groups (including amino groups) in reactions of wool and wool products, recourse has been made to the use of β-naphthoquinone-4-sulfonic acid. Treatment of wool with hot alkalies developed its reactivity with the quinonesulfonate. Wool, after treatment with cold sodium hydroxide (90° Tw.) showed some development of the amido groups, thus accounting for its increased affinity for acid dyes. A short treatment with a hot mixture of equal parts of sulfuric acid and water until the wool began to gelatinize greatly increased the extent to which the naphthoquinonesulfonate would condense. In all cases investigated the connection between the development of amino groups and increased affinity for dyes is clearly intimate. Wool boiled with dilute sodium bisulfite gains in affinity for acid dyes. The effect of severe steaming is to increase affinity for acid dyes and also amination.

102.—The Nitrogen Content of Natural and Processed Wools.

J. Barratt. *J. Soc. Chem. Ind. 47,* T69-72 (1928). Analytical methods and results are given. With the exception of the colored samples, natural wools varying widely in quality of fiber and locality where grown show little variation in nitrogen content. The average value is 16.72 per cent. The nitrogen content of the colored samples decreases with increasing color contrast, which suggests the presence of a pigment of lower nitrogen content than that of normal wool. The general effect of alkali is to increase the nitrogen content, that of acid to decrease it. The portion of wool substance removed by chlorination and also by chlorination followed by treatment with dilute ammonia solution appears to have a similar nitrogen content to that of the remainder.

103.—Amino-Nitrogen Content of Wool and Collagen.

J. R. Kanagy and M. Harris. *J. Research NBS 14,* 563-74 (1935), RP787. Results show that, when wool, collagen and arginine are treated with nitrous acid, increasing amounts of nitrogen are evolved with time, and this is due to the action of nitrous acid on the guanidine nuclei. Since the evidence indicates that nitrogen from the guanidine group is not free amino nitrogen, the amino-nitrogen content of the wool and collagen are corrected for the guanidine nitrogen evolved. Values of 2.53 per cent of the total nitrogen as amino nitrogen in wool and 2.77 per cent for collagen were obtained.

See 86, 98, 147, 148, 206, 266, 281, 282, 342.

Sulfur.

104.—Is the Sulfur in Wool Combined With Oxygen?

E. Grandmougin. *Chem.-Ztg. 31,* 174 (1907). The keratin of wool probably contains the sulfur combined with carbon and hydrogen, as keratin and proteids give similar products on hydrolysis and those from proteids are known to contain the sulfur in this condition. Raikows (*Ibid.* 900 (1905)) reported the production of sulfur dioxide when wool was treated with phosphoric acid, but the author failed to get a trace of it from unbleached wools.

105.—The Existence of Sulfur United to Oxygen in Wool.

P. N. Raikow. *Chem.-Ztg. 31,* 539 (1907). Negative results obtained by Grandmougin (*Ibid. 31,* 529) led the writer to repeat former experiments. Upon digesting washed but unbleached white and brown wools with syrupy phosphoric acid in closed

flasks for five weeks at the ordinary temperature, the wool nearly all dissolved, and upon opening the flasks a strong odor of sulfur dioxide was perceptible. This, he believes, confirms the theory that part of the sulphur in keratin is united to oxygen.

106.—Sulfur in Wool Bound in Sulfitic Form.

H. Strunk and H. Priess. *Z. physiol. Chem. 76,* 136-44 (1912). The observations of Raikow that wool kept in contact with syrupy phosphoric acid gives rise to small amounts of sulfur dioxide were confirmed. The quantity of sulfur dioxide obtained (0.0064 g. from 300 g. of wool) was far too small to permit the conclusion that a portion of the sulfur in the keratin molecule is bound to oxygen in the sulfitic form. It was found that dry wool has a strong affinity for hydrogen sulfide, which may be readily oxidized to sulfurous and sulfuric acid. This would account for some of the contradictory results. The presence of minimal quantities of sulfuric acid in natural wool might, therefore, be readily accounted for.

107.—The Determination of Sulfur in Wool.

M. C. White. *Proc. S. Dak. Acad. Sci. 3,* 43-5 (1919). Digest 1 g. wool with sodium hydroxide and lead acetate, acidify with acetic acid and further digest, filter and wash the precipitated lead sulfide. Decompose the lead sulfide and the filter paper with hydrochloric acid, concentrate, make alkaline with sodium hydroxide and then acidify with acetic acid and filter. Determine the lead in the filtrate as chromate in the usual manner. Then determinations yielded unusually concordant results. The method was compared with various other methods described in the literature and found to be superior.

108.—The Sulfur Content of Wool. I. Inherent Variations According to the Type of Wool.

J. Barratt and A. T. King. *J. Textile Inst. 17,* T386-95 (1926). Analytical methods and results are given for the determination of sulfur in wool. The Carius method is regarded as the best. There are inherent variations in the sulfur content according to the type of wool. Generally the finer wools contain more sulfur. There are also definite variations between different wools of the same quality and breed, and in pedigreed flocks the sulfur content of the wool varies with different animals. Variations in sulfur content occur in different parts of the same fleece. Kempy wools show a lower sulfur content than non-kempy wools. The lowest sulfur value was obtained from a sample of coarse Turkey mohair.

109.—The Sulfur Content of Wool.

S. R. Trotman and H. S. Bell. *J. Soc. Chem. Ind. 45,* T10-2 (1926). The sulfur content of wool as given in the literature ranges from 0.5 to 5.4 per cent. The object of this study was to determine if such differences actually exist in samples of known origin and purity. The wide differences hitherto reported in the sulfur content of wool are caused largely by the different methods of analysis. The various methods for the determination of sulfur in organic material were examined critically, and their actual or possible errors are indicated. The method of analysis adopted was that of Benedict-Denis (cf. *C. A. 5,* 114, 1287, 1448) modified as follows: About 0.2 g. of wool is warmed with a little sodium hydroxide solution made from metallic sodium, till it is just dissolved. A few drops of bromine are added and after a few minutes the solution is neutralized with nitric acid; 10 ml. of the Benedict-Denis reagent is then added and the determination is completed according to the Benedict-Denis procedure. The sample of wool for analysis is purified by extraction in a soxhlet apparatus with petroleum ether and alcohol and then washed with hot water. The results on a sample of "Botany web" ranged from 3.06 to 3.30, average 3.19 per cent of sulfur. The unmodified Benedict-Denis method gave 3.24 per cent sulfur. The narrow limits of variation in the sulfur content of wool would be expected if keratin or wool protein is a definite chemical compound.

110.—Utilization of Sulfur by Animals.

T. Brailsford Robertson. *Australia Council Sci. Ind. Research Bull. 39,* 5-51 (1928). This is a detailed review of the literature with complete bibliographical references. The article contains an excellent review of the history of cystine and other sulfur-containing amino acids, and the relation of these sulfur-compounds to the nutrition of sheep, with especial emphasis on the importance of sulfur-containing amino acids in the growth of wool.

111.—Utilization of Sulfur by Animals.

H. R. Marston and T. B. Roberston. *Australia Council Sci. Ind. Bull. 39,* 5-51, (1928). A review of the literature dealing with sulfur metabolism compiled with the object of laying a foundation for research into the problem of the economic importance of sulfur in wool production.

112.—The Sulfur Content of Wool. II. Distribution of Sulfur Along the Fiber, Variation With Color and the Effect of Exposure to Ultra-Violet Light.

J. Barratt and A. T. King. *J. Textile Inst. 20,* T151-8 (1929). In a majority of the samples examined the highest percentage of sulfur was found to be toward the tips. This distribution was not affected by a typical sulfur-containing dip. Weathering causes a diminution of sulfur in the most exposed parts of the fiber. White wool has a higher sulfur content than black. Cleaned samples exposed for 80 to 100 hours to the light from a quartz lamp lost from 3.7 to 5.0 per cent of their sulfur content. If irradiation was followed by treatment with 0.001 *N* sodium hydroxide, this loss was more than doubled. Microscopic examination showed that the scales were raised and some completely removed. It is suggested that these scales possess a higher sulfur content than the cortex; hence a decrease in the number of scales would explain in part the loss of sulfur on irradiation. This paper contains an addendum in which the authors criticize similar studies by H. R. Marston who reported no inherent variations in sulfur content. The biological significance of the variable sulfur content of wool is discussed, and the belief advanced that this property is due to variations in the incorporation of cystine nucleus under the action of glutathione. III. Effects of chemical processing such as scouring, liming, and chlorination as conducted by the authors have little effect on the total sulfur content. With respect to scouring with sodium carbonate and alkali soaps, this conclusion contradicts that of Marston.

113.—Relation Between Cystine Yield and Total Sulfur in Wool.

C. Rimington. Leeds. *Biochem. J. 23,* 41-6 (1929). Wools differing in sulfur content from 3.34 to 4.08 per cent and fine and coarse samples of Turkey mohair are all capable of yielding their entire sulfur as cystine when hydrolyzed by acids.

114.—The Nature and Condition of the Sulfur in Wool.

G. Salomone. *Bol. lanicra 43,* 992-5 (1929). Sulfur is a constituent of wool, and when eliminated the structure and tenacity of the fiber are changed. If the wool is treated with dilute alkalies to eliminate a small part of the sulfur there is a change indicated by Beck's stannous chloride reagent or Pauly's diazobenzenesulfonic acid solution. Acids and alkalies produce cystine, cysteine, thiolactic acid, thioglycol, ethyl sulfide, methyl and ethyl mercaptans and hydrogen sulfide with wool. Cystine predominates. Some of the other compounds come from the decomposition of cystine. A part of the sulfur in wool is present as bisulfide or organic sulfide, and a part in different combinations. The presence of sulfur compounds in wool is proved by the easy oxidation of a portion

of these. When wool is exposed for a long time to ultraviolet rays it becomes slightly acid, from formation of sulfuric acid. The sulfur atoms in wool are therefore not all combined in the same way; there are two different sulfurized protein complexes, one with sulfur easily decomposed by weak alkalies and oxidizing agents, and the other with sulfur of strong stability, only detached when the total decomposition of wool is brought about with warm concentrated nitric acid, saltpeter or sodium peroxide in a melted condition.

115.—The Sulfur of Wool Proteins.

S. R. Trotman. *Textile Recorder 47,* 70 (1929). The wide variation in the sulfur content of wool found by different investigators is ascribed to the fact that: the methods of analysis are faulty; the sulfur is not wholly a constituent part of the protein molecule; wool consists of two or more proteins containing different proportions of sulfur; the proteins are readily broken down, with the splitting off of compounds containing sulfur. These possibilities are briefly discussed.

116.—Note Upon the Sulfur Linkage in Wool.

C. Rimington. *Biochem. J. 24,* 205-7 (1930). The sulfur groupings in wool are less reactive than would be expected from such compounds as cystine peptides and anhydrides. Free disulfide or sulfhydryl groups are not present in undamaged wool.

117.—Method for the Determination of Sulfur in Wool and Similar Materials.

C. Rimington. *J. Soc. Chem. Ind. 49,* T139-40 (1930). The method is an application of the Benedict-Denis method for determining sulfur in urine. Dissolve approximately 0.25 g. of material in 10 ml. of strong hydrochloric acid, add 5 ml. of Benedict-Folins reagent. Evaporate and ignite the residue. Organic matter and sulfur are oxidized and the sulfur is then precipitated with barium chloride in the usual way.

118.—Note on the Sulfur-Free Nature of Medulla in Blackface Wool.

J. Barratt and A. T. King. *Biochem. J. 25,* 1075-6 (1931). The sulfur content of the medulla substance is low in comparison with that of scale and cortex.

119.—Sulfur Distribution in the Component Structures of Wool and Porcupine Quills.

J. G. Barker and A. T. King. *Biochem. J. 25,* 1077-80 (1931). The sulfur content for the whole quill is 10 per cent lower than that for the crotex. The various components of wool fiber may be summarized thus: Scales: cystine, positive; tyrosine, negative. Cortex: cystine, positive; tyrosine and histidine, positive. Medulla: cystine, negative; tyrosine, positive. The staining effects with both wool and quill sections point to the view that the medulla cells do not contain sulfur.

120.—The Sulfur Content of Some New Zealand Wools.

D. J. Sidey. *J. Textile Inst. 22,* T370-3 (1931). Data are given on the sulfur content of a series of wools of known history grown under similar conditions. The samples were selected in pairs, one for its good spinning properties, the other being indifferent in this respect, while all the other factors and characteristics were kept as nearly alike as possible. The results indicate that there is a relation between spinning quality and sulfur content, the better spinning wool having a higher sulfur content.

121.—The Sulfur Content of Wool. IV. Further Evidence of the Variable Sulfur Content of Wool.

J. Barratt and A. T. King. *J. Textile Inst. 24,* T119-21 (1933). In view of Marston's conclusion that the sulfur content of wool is constant, the sulfur contents of wools purified by the methods of Marston and of the authors were compared, and the sulfur contents of a series of Scotch half-bred wools were determined. The results confirm the authors' original conclusions that the sulfur content of wool is variable and is not affected by the purification method. The variation in the sulfur content of the base and tip portions of the fiber is also demonstrated.

122.—Reactivity of the Sulfur Linkage in Wool.

J. B. Speakman. *Nature 132,* 930 (1933); H. J. Woods, *Nature 132,* 709 (1933). From the contraction of wool fibers in solutions of sodium sulfide and silver sulfate, it is apparent that the phenomenon of supercontraction is associated with the breakdown of disulfide linkages in wool, so that when strained fibers are exposed to steam, the first reaction is $RSSR + H_2O \rightleftharpoons RSH + RSOH$. That this reaction is possible is supported by the fact that wool heated with water in the presence of mercury vapor is rapidly contaminated with mercuric sulfide at a temperature as low as 55°. The second step, the rebuilding of new linkages, probably takes place as follows: $RSOH + RNH_2 = RSNHR + H_2O$. This view is supported by the fact that when fibers are treated with a solution of saturated silver sulfate for 17 hours in the cold, to convert the disulfide group to RSO_2H, their ability to assume a permanent set is considerably reduced. The reactivity of the sulfur linkage in wool is also shown as follows: Prolonged treatment with baryta water removes the sulfur from wool, but an additional compound is apparently formed first. Its formation is responsible for the inability of fibers treated with saturated barium hydroxide for 1.5 hours in the cold to contract when boiled 1 hour with a 5 per cent solution of sodium bisulfide. In addition such fibers have no power of assuming a permanent set.

123.—The Sulfur Content of Merino Wool.—Its Distribution and Relation to Fineness and Quality.

F. N. Bonsma and P. J. Joubert. *S. African J. Sci. 31,* 347-70 (1934). Results show that the sulfur content varies with different individuals and is primarily dependent upon hereditary factors, but in general a gradual increase in sulfur occurs from fore- to hindquarters. A deficiency of cystine in the diet of the animal definitely lowers the sulfur content of the wool. This depression is associated with a wool, poor in substance, which indicates incomplete keratinization of the entire fiber plasm. A correlation of 0.0572 was found between the sulfur content and fineness of the wool.

124.—Determination of Sulfur and Sulfate in Wool.

R. T. Mease. *J. Research, NBS 13,* 617-23 (1934), RP731. The total sulfur is determined by completely oxidizing a 0.5-g. sample of the dried or conditioned wool in an oxygen bomb under 150 to 80 lb./sq. in. pressure with ammonium carbonate and precipitating with 10 ml. of a 5 per cent solution of barium chloride. The sulfate is determined by heating, at 94 to 100°, 1 to 1.5 g of the wool in a test tube of 75 ml capacity to which 20 ml. of a 30 per cent (by weight) of hydrochloric acid has been added. After solution is complete (20 to 30 min.) it is diluted with an equal volume of water, filtered and the sulfate precipitated with 10 ml. of a 5 per cent solution of barium chloride.

125.—Sulfur in Wool.

A. T. King. *J. Textile Inst. 25,* 33-42. (1934). The relationship of the sulfur content of wool to the part it plays in the structure and processing properties of wool is discussed.

126.—The Potential Reducing Properties of Wool. I. The Behavior of Wool in Presence of Water and Al-

kaline Liquids. The Sulfur Groups in Wool.

E. Clayton. *J. Soc. Dyers Colourists 52,* 86-95 (1936). The behavior of wool in the presence of certain polar liquids was studied; evidence was found that, although the fiber develops mild reducing properties in the presence of water at the boiling point, any really effective action in practice is dependent on break-down of the molecule. Apart from slight swelling phenomena, wool is not appreciably affected either physically or chemically by water at 100°, although long boiling results in the development of a yellowish brown color on the fiber, while slight modification of the scale structure and loss of strength may occur with evolution of traces of hydrogen sulfide. Most of the wool-liquid reducing systems met with in practice are caused by the conversion of a varying amount of the sulfur of the fiber into an active-ionic state. Tests on ordinary boiled, also steamed, wool gave no evidence of the presence of sulfhydryl groups. The wool fiber is built up mainly of two polymeric forms of the same sulfur-containing protein, and it is assumed the outer scales constitute the higher polymer and the cortex the lower polymer. Any alkaline salt exerts a rapid incipient attack on the molecular structure of wool at 100° without any apparent alteration in the structure. Successive boilings with fresh water show diminished evolution of hydrogen sulfide until it ceases altogether. The main sulfur linkages are attacked slightly by boiling mildly alkaline solutions; this indicates that sulfhydryl groups are not developed from disulfide links in the wool complex by treatment with boiling water. Boiling for 30 seconds in 1 per cent borax solution containing a little lead carbonate in suspension causes the wool to turn slightly brown, whereas when the same type of wool is boiled in distilled water containing lead carbonate for a similar period no appreciable alteration in color occurs. This test might be used for detecting the presence of traces of alkali in scoured wools.

127.—The Reactivity of the Sulfur Linkage in Animal Fibers. I. The Chemical Mechanism of Permanent Set.

J. B. Speakman. *J. Soc. Dyers Colourists 52,* 335-46; *J. Textile Inst., 27,* 231-43 (1936). An attempt is made to determine which linkage takes place and to establish the chemical mechanism between peptide chains, side linkages, cystine, and the salt and side chains of hydroxy acids. It is concluded that the permanent set acquired by strained animal fibers in steam is due to consecutive reactions. Internal stress is first dissipated by rearrangement of hydrolyzed salt linkages. The fibers can collapse when released in steam to a length less than the original length. Such collapse is prevented by prolonged steaming, which leads to the rebuilding of new linkages between the peptide chains. The free amino groups of arginine and lysine side chains and the products of hydrolysis of the cystine linkage play an essential role in the rebuilding processes. Since the linkages resist the action of boiling water, boiling 0.1 *N* acid, alkali, and boiling sodium bisulfite, they are doubtless formed according to the equation: $RSOH + RNH_2 \rightarrow RSNHR + H_2O$. In general, the setting process is associated wth compounds which facilitate break-down of the cystine link and give decomposition products capable of condensation with amino groups. Hydrolysis of the main peptide chains must be avoided.

128.—The Chemistry and Metabolism of Compounds of Sulfur.

V. du Vigneaud and H. M. Dyer. *Ann. Rev. Bochem. 5,* 159-80 (1936). This review deals with sulfur compounds, in the following relations: newly isolated compounds, syntheses, role in biological oxidation-reductions, analytical methods, cystine content of isolated proteins, glutathione in blood and tissues, relation of diet to tissue composition, absorption and oxidation in vivo, cystinuria, mercapturic acid, sulfhydryl and disulfide compounds in cellular growth and cancer, growth of hair and wool, in micro-organisms, relation to selenium.

129.—State of the Sulfur in Oxidized Wool.

M. Harris and A. L. Smith. *J. Research NBS 18,* 623-628 (1937). During treatment with oxidizing agents, the disulfide sulfur in wool appears to be changed to higher states of oxidation. The existence of oxidation derivatives of the disulfide compounds is indicated by the alkali-solubility determination, the lead acetate test, by reduction with hydrochloric acid-potassium iodide solutions, and by cystine analyses. The intermediate oxidation derivatives of cystine are unstable under the conditions necessary for protein hydrolysis, and at least one of them, cystine disulfoxide, is partially converted to cystine. The results indicate that the values obtained for the cystine content of oxidized wool may be expected to be higher than the actual cystine content, since they represent the amount of cystine formed from the partially oxidized cystine compounds as well as from unoxidized cystine.

See 41, 51, 59, 62, 85, 86, 94, 95, 98, 147, 194, 201, 262, 264, 265, 278, 291, 300, 305, 306, 312, 320, 342, 353, 354, 358.

CHLORINATION (See halogenation).

Also 40, 131, 134, 135, 140, 148, 156, 157, 158, 320, 354, 386.

CYSTINE (See Chemical Constitution—Amino Acids).

Also 110, 113, 114, 116, 119, 127, 128, 129, 156, 306, 348, 352, 354, 356, 357, 358.

DAMAGE, Determination of (See Light, Oxidation. etc.).

130.—Two Analytical Aids for Controlling the Manipulation of Wool.

M. Becke. *Farber-Ztg. 23,* 45-8, 66-71 (1912). To determine the amount of wool-substance which is dissolved by a given process, Becke uses the biuret reaction. A color scale for comparison is made as follows: Prepare a standard solution of wool-substance by dissolving 1 g of wool in 50 ml *N* sodium hydroxide and heating on the water bath. Add 200 ml of distilled water and 50 ml of *N* hydrochloric acid to neutralize the sodium hydroxide. Boil the solution for a quarter of an hour to remove the hydrogen sulfide and if any wool-substance precipitates, take it into solution with 5 to 10 ml of *N* sodium hydroxide. After the solution cools, make up to a volume of 500 ml. Place in each of 10 similar tubes the proper amount of standard solution of wool-substance to give a graded series containing from 1 to 10 mg. of wool-substance, making the volume 5 ml in each case by the addition of distilled water. To each tube 5 ml of normal sodium hydroxide and 1 ml of normal copper sulfate are added. The solution to be tested is treated in the same way, having first been diluted or concentrated on the water bath, if necessary, so that the color obtained will fall within the range of the standards. Allow the precipitate to settle out, and then make the comparisons (1 hr.). The standard solution of wool-substance and the color standards are satisfactory for use for 3 to 4 days. Since different samples of wool give slightly different color scales, the standard solution should preferably be made from the wool being used. Wool which has been treated with alkalies is colored yellow to brown when treated with a hot solution of stannous chloride and acetic acid. The intensity of the color depends upon the extent to which the wool has been attacked by the alkali. The test is performed as follows: 5 g of the wool is put into a flask containing 200 ml of acetic acid 10 per cent and 5 to 10 per cent stannous chloride, calculated on the weight of the wool, are added. The temperature is maintained at 90 to 95° for ½ to ¾ hour, and the comparisons are then made. Becke has used these two methods in making a

comparative study of the effects of various sizing, dyeing, and washing processes.

131.—The Properties of Wool and a New Chemical Method for Detecting Damaged Wool.

K. von Allwörden. *A. Angew Chem 29,* I, 77-8 (1916). Between the external plate-cells (scales) and the fiber cells (body of the fiber) there is a substance which the author names elasticum. The characteristics of the fiber are largely determined by this substance. If all of this substance is removed, the fibers are no longer capable of being felted or finished properly and are brittle and weak. Elasticum, which is soluble in alkalies, is a carbohydrate, the osazone of which may be prepared readily. In 8 L of 2 per cent sodium hydroxide there is suspended 500 g of factory-scoured wool, previously rinsed with warm distilled water. After standing for 24 hours at a temperature of not more than 25°, practically all of the elasticum will have dissolved, together with some albuminous substances. Since the former is dialyzable, it may be separated from the mixture. The solution of elasticum thus obtained is acidified with acetic acid and concentrated to 200 ml. Sodium acetate and phenyl-hydrozine are then added, and the mixture is heated in boiling water. Microscopic needles separate after ½ to 1 hr. The imperfectly purified osazone melts at 188°. The reduction of Fehling solution by elasticum is effected only after separation of albumin, a fact which explains previous failures to detect it. Its reducing action accounts for the reducing properties of wool. The content of elasticum determines the value of wool, and manufacturing processes should be designed to conserve it. The fiber-cells proper are more easily attacked by acids than the plate-cells, and elasticum, which is insoluble in acids, is able to protect mechanically the underlying fiber. This fact is of importance in carbonizing and acid-dyeing. Gravimetric determination of elasticum should give an indication of the properties of the fibers. Optical methods, osazone determination or copper reduction are suggested, but none has been worked out. Chlorine water is a valuable reagent to show the presence of elasticum. The plate-cells are not easily attacked by chlorine while the fiber-cells and elasticum react readily. The swelling caused by the reaction of the latter forms globular enlargements on the fibers, the plate-cells being distended. The wool fiber is placed upon a slide and covered with a few drops of water. An equal volume of chlorine water is then added. The fiber should be viewed under a microscope at a magnification of about 200x. Dynamometric tests are little affected by removal of elasticum, while the wearing qualities of the fabric are greatly impaired. This conclusion was proved by an examination of a number of uniforms which had been unsatisfactory in service. Damage developing during acid-dyeing is often the fault of the scouring rather than of the dyeing. Bottoming in an alkaline vat followed by topping with acid dyes is objectionable. Spots are often formed as a result of the reducing action of elasticum.

132.—A Chemical Test for Injury to Wool Fibers.

O. Sauer. *Angew. Chem. 29,* I, 424 (1916). The method devised by Sauer depends upon treating various samples of wool with a reagent which effects partial solution of the wool-substance, and noting differences in wools which have been previously subjected to various processes such as are used in the textile industries. Approximately 0.5 g of wool is put into a 200 ml volumetric flask, and covered wtih 40 ml water, 50 ml of 1 per cent hydrogen peroxide and 10 ml of 0.5 potassium hydroxide solution. The flask is closed with a modified Peligot tube which is filled with water to prevent loss of ammonia. After 3 days' standing, the mixture having been shaken once daily, the flask is filled to the mark with distilled water. After thorough mixing, 100 ml is filtered off, and after the addition of excess of sulfuric acid is reduced in volume before making a nitrogen determination. The percentage of nitrogen, calculated on the weight of wool taken, is called the "soluble nitrogen" number. The total nitrogen in 0.5 g of the wool is determined by the Kjeldahl method. The water content of the wool may be disregarded, if the weighings of the samples for the two tests are made consecutively. The ratio of "soluble nitrogen" to total nitrogen is found to vary considerably with the chemical treatment to which the wool has been subjected in manufacture. Samples of wool which were exposed under glass during 4 summer months showed an increase in "soluble nitrogen" number. Dyed wools have their "soluble nitrogen" number increased less by such exposure than undyed wools of the same lots. The following values were found, the percentages being the fraction of the total nitrogen which is dissolved under the conditions of the test. Undyed wools, not exposed to light: 13.3 per cent and 11.9 per cent; dyed dark olive, unexposed 17.9 per cent and 15.3 per cent, respectively. The values for the same wools after exposure; undyed, 44.5 per cent and 52.1 per cent; dyed dark olive, 26.0 per cent and 33.3 per cent.

133.—Further Application of the Biuret Reaction to Wool.

M. Becke. *Farber-Ztg. 30,* 128-30 (1919); *13,* 2603. The stannous chloride reaction gives only partial information concerning the injury done to wool fibers by alkaline solutions. The biuret reaction, however, yields exact numerical data on the quantity of wool-substance dissolved by acids, alkalies, soap, etc. Between the loss by dissolving of wool-substances thus determined and the decrease of tensile strength and elasticity of the yarn, etc., there is a close relationship. The biuret reaction, therefore, supplements these dynamometrical tests, and is even more sensitive for detecting small changes in the wool. Sulfuric acid has a marked hydrolyzing effect upon wool. The basic substances formed dissolve in the acid solution, while the acid products are dissolved readily by subsequent treatment with alkaline solutions. High temperatures, increased time of action, and increased concentrations, of the acid favor the hydrolysis. Contrary to the prevailing opinion that dyeing in acid baths is the least injurious to wool, dyeing with sulfuric acid and Glauber salt or with sodium bisulfate is very harmful, since it renders the wool susceptible to attack by subsequent treatment with water, soap, sodium carbonate, sodium hydroxide, etc. While preliminary treatment with sulfuric acid increases the solubility of wool in alkaline solutions, a preliminary treatment with alkalies (of reasonable concentrations) does not facilitate the attack by sulfuric acid solutions.

134.—Wool. Causes of the So-Called "Allwörden's Reaction."

P. Krais and P. Waentig. *Neue Faserstoffe I,* 265-6 (1919). Allwörden's reaction does not give uniform results with all kinds of wool, and different sections of the same wool fiber behave differently. The chlorine water must be freshly prepared; with bromine water the swellings separate better from the fiber. The removal of suint and grease is important. Hairs containing a medulla may show the reaction very distinctly; feathers do not react. Both in the chlorine reaction which causes the formation of the swellings and in the treatment with alkali which removes the "elasticum" from the wool, there is an attack on the proteins of the wool. The substance sensitive to chlorine is a protein present in the fibrilla layer or in a cementing substance adhering to the fibrilla. At high temperatures the sensitiveness of the test to the influence of alkalies increases to an extraordinary degree so that at the boiling temperature the traces of alkali which are dissolved from an ordinary glass vessel are sufficient to cause the

absence of the reaction. The effect of boiling, however, is entirely suppressed by traces of acid, and the reaction remains positive after an acid treatment which would certainly have an injurious effect on the quality of the wool.

135.—Allwörden's Reaction.
W. Spöttel. *Textilber. 6,* 605 (1925). The phenomena exhibited by chlorinated wool are explained by changes in the superficial scales.

136.—Low-Grade and Damaged Wool and the Detection of Damage in Woolen Fabrics.
S. R. Trotman. *Textile Recorder 43,* 70-1 (1925). When proteins (wool) are acted on by reagents or enzymes, hydrolysis occurs, changing the complex colloid into a less complex and ultimately non-colloidal compound soluble in neutral, alkaine, or acid solutions. The incipient decomposition of wool is not visible microscopically. It possibly proceeds: proteins, proteosos, peptones, polypeptides, amino acids. Damage may be detected by the biuret or other reactions of proteoses and peptones; the elasticum reaction, or Krais and Waentig's modification, or by Beck's stannous chloride reaction.

137.—Deterioration of Dyed Wool on Exposure to the Atmosphere.
H. Lagache. *Tiba 5,* 1479-87 (1927). This is a review of work done in Germany on the effects on wool of the nature of the dye and process of dyeing.

138.—A Method for Detecting Damaged Wool.
W. Sieber. *Melliand's Textilber. 9,* 326-8 (1928). Damaged wool has been detected by the biuret reaction, by the estimation of nitrogen compounds soluble in potassium hydroxide, and by Allwörden's reaction using phosphotungstic acid. A newer method is based on the dyeing of tyrosine with alkaline diazo solution. This can be prepared as follows: 2 g sulfanilic acid, 3 ml of water and 2 ml of concentrated sulfuric acid are added slowly to 1 g of sodium nitrite in 2 ml of water. This is filtered and dissolved in 10 per cent sodium carbonate. Although the reagent decomposes rapidly, it dyes only the tips of undamaged wool red, while wool which has been attacked with alkali or acid, or which has been excessively damaged mechanically, is uniformly colored. Similar results may be obtained more conveniently by use of a 1 per cent solution of benzopurpurin. Photomicrographs are reproduced.

139.—The Detection and Control of Damage of Wool.
S. R. Trotman. *Ind. Chemist 4,* 118-9 (1928). This is a review of the literature.

140.—A Technic for the Microscopical Examination of Wool Fibers.
R. Burgess and C. Remington. *J. Roy. Microscop. Soc. 3,* 49, 341-8 (1929). Where damage to the epithelial scales permits penetration, an alkali solution of diazobenzenesulfonic acid (Pauly's reagent) stains wool fibers brownish red because of a reaction with the tyrosine and histidine of the cortex. Defects from various causes, such as injuries to the wool on the sheep or in shearing, skin wool, or low grades of fiber, are made evident. Damage in chlorination or from microörganisms is revealed. The resistance of "processed" wools to injury depends on the intactness of the scales.

141.—Recognition of Chemical Damage of Wool.
P. Krais and V. Schleber. *Leipzig. Monatschr. Textil. Ind. 44,* 165-7, 211-5 (1929). Dyeing methods, using, e.g., cotton blue 10B, are preferable to nitrogen determinations and various color reactions of the break-down products of wool, for proving alkali damage. The coarser wools are comparatively resistant to alkali attack. Where such injury has occurred during scouring, there is a serious loss in tensile strength during dyeing in acid baths.

142.—A Quantitative Method for the Determination of "Soundness" in Wool and Cloth.
C. Rimington. *J. Textile Inst. 21,* T237-447 (1930). A weighed sample of wool is treated with Pauly's reagent (diazotized sulfanilic acid), dissolved in 10 per cent of sodium hydroxide solution, and the color intensity of the resulting solution matched against a solution of a standard dyestuff (0.1 per cent new acid brown S). The degree of damage is expressed numerically; the value "100 units of damage" is assigned to a sample of wool such that 0.1 g treated as described, made up to 25 ml final volume, gives a solution of color intensity exactly equal to that of the standard dyestuff. The method is not applicable to dyed or naturally colored material, and is not recommended when the degree of damage is small.

143.—Detection of Damage in Wool with Indigo Carmine.
A. Herzog. *Melliand Textilber. 12,* 768-9 (1931). The mechanically and chemically (e.g., with sodium hydroxide) damaged portions of wool fibers become stained deeply when treated with aqueous indigo carmine, and this staining is more clearly observed microscopically if the fibers are mounted in glycerol. The indigo carmine solution is much more stable than the Pauly reagent, and the stained fibers mounted in glycerol-gelatin mixture are permanent. It is also satisfactory to use aqueous indigo carmine and picric acid; the damaged portions acquire a green color and the normal portions of the wool become pale yellow.

144.—Methylene Blue on Wool.
E. Ristenpart and H. Schwerdtner. *Monatschr. Textil-Ind. 46,* 28-30 (1931); *Chimie & industrie 26,* 159 (1931). This is a study of the test proposed by Kertesz (*C. A. 14,* 1760-1) for detecting the deterioration of wool, with a view to determining if possible the conditions under which it should be carried out to measure the degree of deterioration. In order to be able to judge differences in the shades obtained, the dyeing should be carried out with 0.01 g of methylene blue and 0.01 g of acetic acid. Subsequent tests showed that in bleaching wool with hydrogen peroxide, the presence of 3 per cent ammonia (on the weight of hydrogen peroxide) had no injurious effects, that ammonia alone does not attack wool and that attack by ammonia begins only in the presence of O.36 g or more of hydrogen peroxide. The deteriorated wool showed only insignificant losses in weight and in tensile strength.

145.—Detection and Estimation of Chemical Damage in Wool.
P. Krais. *J. Textile Inst. 23,* P144-6; *Dyer 67,* 578-9 (1932). The classification of the extension curves and a comparison of the breaking strengths of the single fibers in the dry and wet conditions is considered a very good measure of the amount of damage done to the fibers.

146.—A New Microchemical Reaction for Detecting Deterioration of Wool by Acids.
P. Krais and O. Viertel. *Textile Forsch. 15,* 35-9 (1933); *Chimie et industrie 31,* 928. The test can detect deterioration even in its early stages and is applicable irrespective of the previous treatment of the wool. hen wool that has been deteriorated by acid is treated with an ammoniacal potash solution, it first swells, and bubbles form and are liberated. The method consists in observing the phenomena under the microscope with a magnification of 250 to 300 diameters. To obtain comparable results, the time required for liberation of the bubbles is noted, the degree of deterioration being inversely proportional to the time. The above reagent is specific for this deterioration, the reaction also occurs with untreated wools, but the time required is much greater. If the deteriorated film has been more or less completely removed before the test, spherical swellings form on the surface, and the gas is given off much later. The test can be applied even after dyeing the wool.

(To be continued in the next Quarterly Research Number)